

Supramolecular Crystal Engineering:
Design and Synthesis of Novel Persubstituted Aromatic
Host Molecules

by

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DEDICATION

To my Mother, Father and Sister

ACKNOWLEDGEMENTS

I would first of all like to thank my supervisor Dr. David D. MacNicol for all his help and encouragement throughout my Ph.D.

I would also like to thank Dr. Gary Downing for his help in the laboratory during my first two years, Drs. Chris Frampton and Keith Henderson for their X-ray work and also to all the technical staff for helping me out, especially Jim Gall for NMR work; Kim Wilson for microanalysis; George McCulloch for infra-red and TGA data; Tony Ritchie for Mass spectra and Alex Burns for his general help in the lab.

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'For years we have considered nature as the ultimate chemist,
but she is limited to specific building blocks and reactions,
we are limited only by our imagination'.

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SUMMARY

Chapters 1-4 present an introduction into the field of supramolecular crystals. Chapter 1 gives a general introduction into the area of supramolecular chemistry while Chapter 2 concentrates on the more specific field of clathrate chemistry laying down definitions and nomenclature. Chapter 3 talks about the discovery of new host molecules going from chance to specific designing and engineering of hosts. Chapter 4 describes some potential applications for these supramolecular crystals.

The research contained in Chapter 5 details the specific use of symmetry and shape in the design of novel host systems based on persubstituted aromatic cores. Section 5.1 talks about the general methods used to synthesise the thiols and phenols required for the synthesis of these persubstituted aromatics. The first type of aromatic cores examined were those with fused benzene rings, Section 5.2. Both anthracene and triphenylene possess C_2 axial symmetry and so their persubstituted derivatives were examined for inclusion potential. Perthiosubstituted anthracene molecules were prepared by an extension of the interesting reaction of saturated fluorocarbons with thiolate anions. Decakis(cyclopentylthio)anthracene was shown to be a versatile host. The structure of its 1,4-dioxane clathrate has been established by single crystal X-ray analysis. Persubstituted (arylthio) and (aryloxy) triphenylenes

were prepared for the first time. No inclusion compounds were observed for the persubstituted (arylthio) triphenylenes, however, dodecakis(*p*-phenylphenoxy)triphenylene was shown to include 1,4-dioxane and a series of glymes. Single crystal X-ray analysis was carried out on dodecakis(*p*-methylphenoxy)triphenylene and dodecakis(*p*-methylphenylthio)triphenylene to see how these type of molecules pack in the crystalline state.

Section 5.3 introduces a new line of investigation. By binding two pentasubstituted benzenes together by a covalent bond or carbon chain we produced linked Hexa-hosts. An investigation into persubstituted biphenyl (O atom link); benzophenone, benzohydrol and diphenylmethane (1 atom link); 1,2-diphenylethane (2 atom link) and 1,6-diphenylhexa-1,6-dione (6 atom link) showed that, so far, only the 1 atom link cores have shown any propensity to include. Single crystal X-ray analysis has been carried out on the decakis(phenylthio)benzophenone/chloroform/acetic acid clathrate to determine its structure. Decakis(phenylthio)benzophenone has also been shown to include ethane-1,2-dithiol, suggesting that this host molecule could be used as a 'molecular bottle' for this odorous reagent.

An investigation into silicon linked molecules is described in Section 5.4. However, when bis(pentachlorophenyl)-1,1,2,2-tetramethyldisilane is reacted with sodium phenylthiolate in DMEU, at 60°C then

pentakis(phenylthio)benzene is formed, confirmed by single crystal X-ray analysis.

A continued investigation of this reaction has revealed that (i) the electron withdrawing fluorines are required for desilylation and (ii) desilylation occurs before full substitution of the five fluorines by the phenylthio side units. Using this information a modified form of this reaction using chloride anions as the nucleophile instead of phenylthiolate followed by quenching of the anion by the electrophile pentafluorobenzylbromide to give bis(pentafluorophenyl)methane, the precursor to persubstituted diphenylmethane host molecules.

Section 5.5 describes further investigations of pentasubstituted benzenes as hosts and shows that they do not include, probably due to the extra flexibility in the molecule.

Section 5.6 presents further results on hexakis(*p*-hydroxyphenoxy)benzene, the hexa-host analogue of hydroquinone. This is also a form of linking the hexahosts, here through hydrogen bonding. This new investigation concentrates on including hydrogen into its cavities. Hydrogen, which is too small to be included into the hydroquinone cavities, is shown to be stored, if only temporarily, into the hexakis(*p*-hydroxyphenoxy)benzene crystal lattice.

Water has been shown to partially plug the larger cavities and so help to delay loss of the gaseous guest.

Finally, use of preorganisation of cavity in design was attempted by linking of the side-chains of a hexasubstituted benzene. The target molecules could not be isolated but the single crystal X-ray of an intermediate hexakis(3,5-dimethoxyphenoxy)benzene which does not include shows the need for further preorganisation of the cavity as some of the methoxy units point inward and so prevent the need for clathrate formation.

1. SUPRAMOLECULAR CHEMISTRY

The area of supramolecular chemistry is still a young one but it covers a wide area of science from biology (e.g. interaction of enzyme-co-enzyme-substrate complexes) to material science (e.g. organic semiconductors and conductors). It can be defined as 'the chemistry beyond the molecule', based mainly on the chemistry of intermolecular interactions. These interactions can vary from hydrogen-bonding through Π - Π stacking to van der Waals interactions, between a host molecule and its guest.

This host-guest phenomenon can be split into two main areas :

- (1) **Molecular Inclusion:** This is when a guest molecule is included into an already existing cavity (Fig. 1a) [e.g. crowns, cyclodextrins, calixarenes etc.] Usually only one host molecule is involved in the aggregate, hence such complexes are known as unimolecular hosts, and (depending on the solvent) can be seen in solution as well as in the crystal.
- (2) **Crystal Lattice Inclusion:** This is when several molecules of the host compound form extra molecular cavities that allow the incorporation (or inclusion) of guest compounds (Fig. 1b). This is known as Clathrate formation.

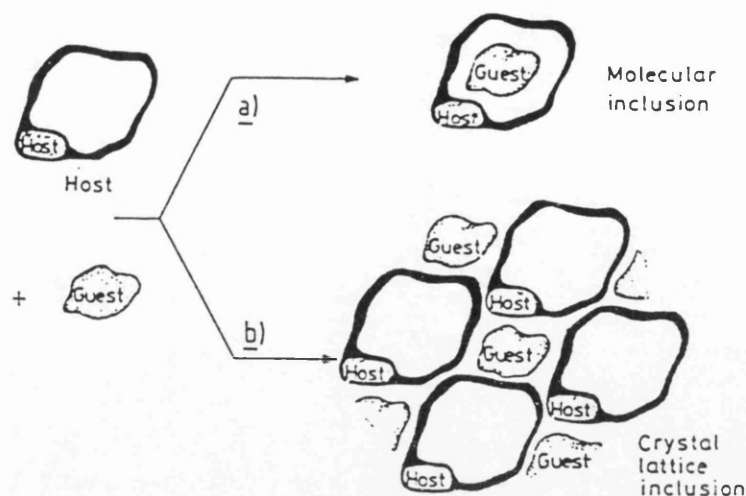


Figure 1¹. The difference between molecular and lattice inclusions: (a) Formation of a molecular complex, where a convex guest fits into the cavity of one host molecule; (b) inclusion of guest molecules into cavities between different host molecules in the crystal lattice (clathrate formation).

1.2 General Nomenclature and Different Types of Host-Guest Aggregates

For classification² of supramolecular compounds we can use 2 main criteria (i) the host-guest interaction (host-guest type) and (ii) the topology of the host-guest aggregate.

There are two extremes of host-guest interaction :

- (1) **Complex:** These are aggregates which are derived from a co-ordination between host and guest components (e.g. crown ethers³).
- (2) **Clathrate (or Cavitare):** These are aggregates where the guest is retained by steric barriers formed by the host lattice (crystal lattice forces) (e.g. urea inclusion compounds⁴).

Between these two extremes there are supramolecular compounds that utilise to a greater or lesser extent both of these interactions, thus borderline cases must be treated as complex / clathrate hybrids (Fig. 2).

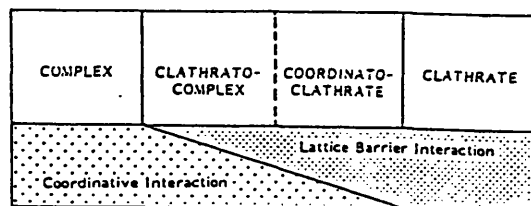


Fig. 2 Assignment of complex / clathrate hybrids⁸

Coordinatoclathrates demonstrate a certain degree of co-ordinative participation but have a dominant clathrate character, e.g. 1,1'-binaphthyl-2,2'-dicarboxylic acid⁵ and clathrato complexes are the other way round, e.g. crown ethers with uncharged molecules⁶.

If we consider topological aspects we can also split these into two extremes.

- (1) Cavitare: These are aggregates which operate via any sort of host cavity (e.g. cyclophanes⁷).
- (2) Clathrate: Extramolecular inclusion in the solid state (see above).

Fig. 3 shows the relationship between complexes, cavitates and clathrates.

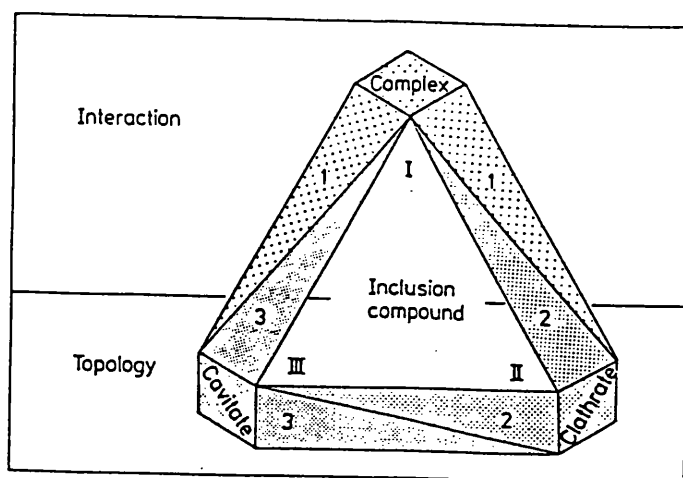


Fig. 3. Classification / nomenclature of host-guest type compounds; definitions and relations: (1) co-ordinative interaction; (2) lattice barrier interaction; (3) mono-molecular shielding interaction: (I) co-ordination-type inclusion compound (inclusion complex); (II) lattice-type inclusion compound (multi-molecular inclusion compound); (III) cavitate-type inclusion compounds (mono-molecular inclusion compound).

We can also define further the type of cavity formed depending on the degree of encapsulation.

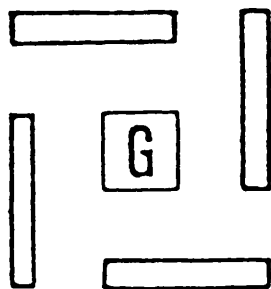
- (a) Layer, sandwich: intercalate e.g. graphite⁹
- (b) Ring: coronate, podate e.g. crown ethers³
- (c) Channel: tubulate e.g. urea⁴
- (d) Pocket, Cleft: Aediculate e.g. Kemp's triacid inclusion molecules¹⁰
- (e) Cage: Cryptates e.g. Dianin's Compound¹¹.

2. CLATHRATES

2.1 Introduction

The emphasis for the main part of this discussion will now move to clathrates and the various ways novel clathrates can be discovered and designed. But first a classification of different types of clathrates will be given in order to facilitate further discussion. Clathrates can be categorised into four types according to their host-guest interaction :

(a)

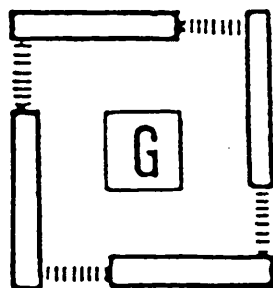


G = Guest

Without any co-ordinative
interaction ('true' clathrate).

Type I

(b)

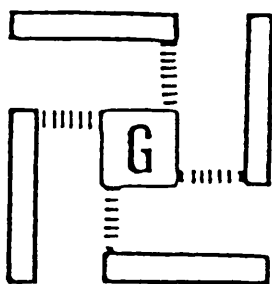


Coordinative host-host interaction

(coordination assisted clathrate

host lattice). Type II

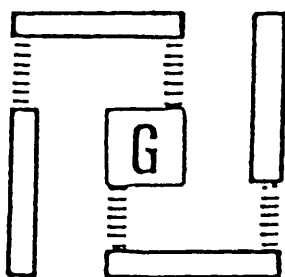
(c)



Coordinative host-guest interaction
only (coordinato-clathrate).

Type III

(d)



Both coordinative host-host and
host-guest interaction (coordinato-
clathrate in a coordination-assisted
host lattice). Type IV

Further classification on the topology of the host-guest aggregate has already been given, however the main types that are encountered in clathrate chemistry are :

(i) Cage

(ii) Channel, tunnel

2.2 Overview of Some Organic Hosts: An Introduction to Preorganisation and Complementarity

Fig. 4 shows a list of some of the most common organic hosts. It is important to notice that they all have two or more of the following properties :

- (i) Symmetry e.g. 2 or 3-fold
- (ii) Intermolecular bonding e.g. H-bonding
- (iii) Rigidity
- (iv) Overall shape

These include the two concepts of preorganisation and complementarity. Preorganisation involves mainly the host and can be defined as factors that help to preorganise the host into an overall shape that enables the lattice to choose a non-close packed alternative and so leave cavities for a guest molecule.

Symmetry may help in preorganisation by amplifying the presence of desirable features, as well as minimising unwanted ones. It also limits how the molecule can pack in the crystal by limiting the number of different orientations in space, therefore reducing the possibility of the molecule adopting a close packed structure. Intramolecular bonding, such as H-bonding, can help preorganisation by interacting with other molecules (e.g. Type II clathrates) and so preventing a close packed structure and lowering the energy of an open structure (e.g. phenol hosts¹²).

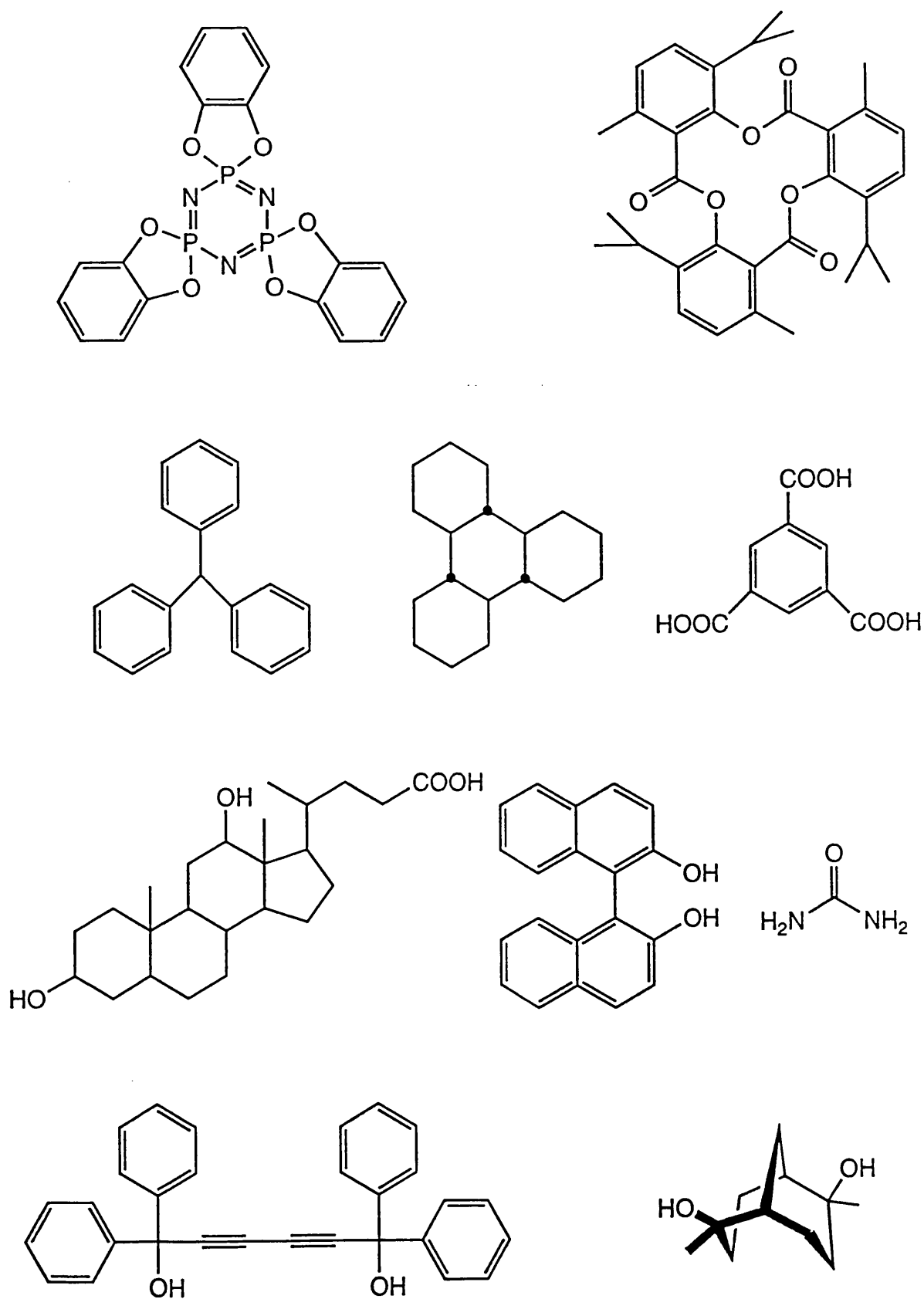


Figure 4 Some common organic hosts.

Rigidity helps in preorganisation by restricting the number of conformers that a molecule can adopt and so limit its ability to obtain any undesirable shapes that might lead to a close packed structure. Shape of the molecule is probably the most important of all these features (the other three factors mainly help to orientate the molecule in the correct fashion or shape). Potential preorganisation of cavities using molecular angularity and concavities is implicit in this type of strategy. Overall aromatic groups are often used as prefabricated walls as they also have the added advantage of rigidity and the ability of utilising certain electrostatic interactions e.g. T-type bonding, Π - Π interactions¹³ etc. (Fig. 5).

All these interactions can not only help the preorganisation of the host but also help in binding the guest. This introduces the idea of complementarity of guest to the cavity. In order to be incorporated (or included) into the host lattice the guest must have not only the correct size and shape but also the correct polarity, orientation, chirality and interactions with the host. This leaves a variety of tools that the chemist can use to design novel host systems. We shall see later how some of these have been utilised.

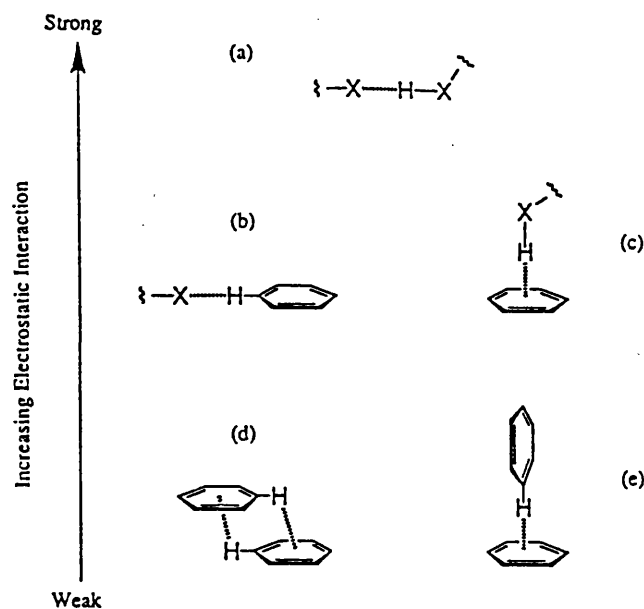


Fig. 5¹⁴. Hierarchy of electrostatic interactions between neutral molecules (X-hetero atom)

- (a) H-bond
- (b) Weak C-H...O H-bond
- (c) Weak N-H... Π H-bond
- (d) Offset Π - Π interaction
- (e) Edge-to-face Π - Π interaction (T-type).

2.3 Discovery of Novel Hosts

There are four main ways that have been used throughout the years, in which novel clathrates have been discovered or designed.

- (1) 1st Generation: Chance

Up until the mid-1970's chance discovery was the main method of discovering new hosts. It is still an important method today.

(II) 2nd Generation: Analogues

This method has been used very successfully (as we will see later) and relies on taking a first generation host and altering it slightly with a view to changing its inclusion ability.

(III) 3rd Generation: Analogy

This was introduced in 1976 when MacNicol used the crystal structure of Dianin's compound and hydroquinone inclusion compounds to design the Hexa-hosts (see later). This is the first of the strategies that involves design.

(IV) 4th Generation: Preorganisation

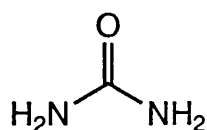
This strategy is pure design, and involves utilising the factors that influence preorganisation (as discussed before) like symmetry, intermolecular bonding, rigidity and shape, in order to design inclusion compounds that have no analogy to other host systems.

In the next chapter we will see how each of these strategies has been used to design hosts.

3. HOST DISCOVERY AND DESIGN

3.1 Ureas

3.1.1 Urea⁴



(1)

Urea (1) was found to form crystalline inclusion compounds with octyl alcohol by Bengen in 1940, by chance (so making it a 1st Generation host). Subsequent work revealed that inclusion compounds were readily formed with *n*-alkanes and *n*-alkenes provided the hydrocarbon has six or more carbon atoms^{15,16}. Urea forms clathrates with a vast number of different guests including hydrocarbons and their alcohols, esters and ether derivatives, also with aldehydes, ketones, carboxylic acids, amines etc. provided their main chain consists of six or more carbon atoms and the chain is not branched. Normally pure urea crystallises tetragonally. However clathrates crystallise in a hexagonal crystal structure (Fig. 6) to form channels.

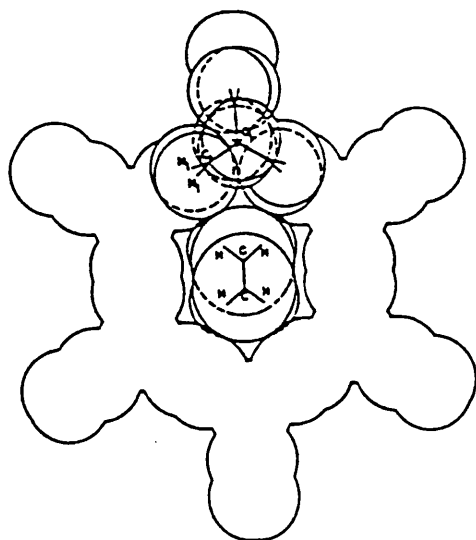


Fig. 6 Cross section of the urea-*n*-hydrocarbon inclusion compound.

A fundamental feature of the channels in the urea lattice is the fact that urea molecules making them up are aligned either in left-handed or right-handed helices (Fig. 7), which are related as image and mirror image. The achiral urea therefore spontaneously crystallises into one of two enantiomorphic lattices.

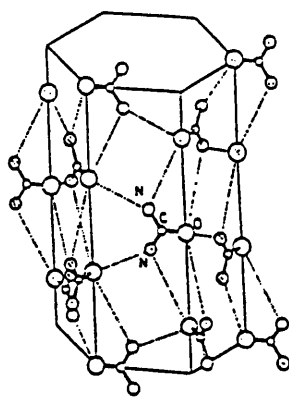
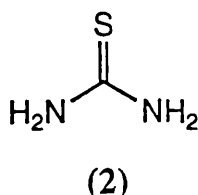


Fig. 7. Schematic representation of an urea clathrate lattice

Almost all urea clathrates form this hexagonal crystal structure, which is a Type II host (coordination-assisted clathrate host lattice involving H-bonding between host molecules). However it has recently been reported¹⁹ that urea forms zigzag channels when sebaconitrile is included. This is thought to be caused by the host H-bonding to the nitrile groups and so this is a Type IV host (coordination clathrate in a coordination-assisted host lattice, involving host-host and host-guest H-bonding).

3.1.2 Thiourea



In 1947, Angla reported that thiourea (2) also formed adducts with a variety of organic compounds²⁰. These clathrates were in general rhombohedral crystals of the coordination-assisted type, similar to urea (Type II). The main difference between thiourea and urea is the larger cavity size of the thiourea clathrate (Fig. 8). The thiourea host lattice has a channel diameter of approximately 7.1Å compared with 5.2Å for the urea host lattice. As a consequence, thiourea forms channel type clathrates with highly branched hydrocarbons e.g. trimethylpentane and larger cyclic compounds such as cyclopentane, cyclohexane and decalin. On the other hand *n*-paraffins cannot

form inclusion compounds with thiourea because of their loose fit in the larger cavities.

It should be noted however that although the structures between (1) and (2) are similar, no spontaneous resolution is observed with thiourea.

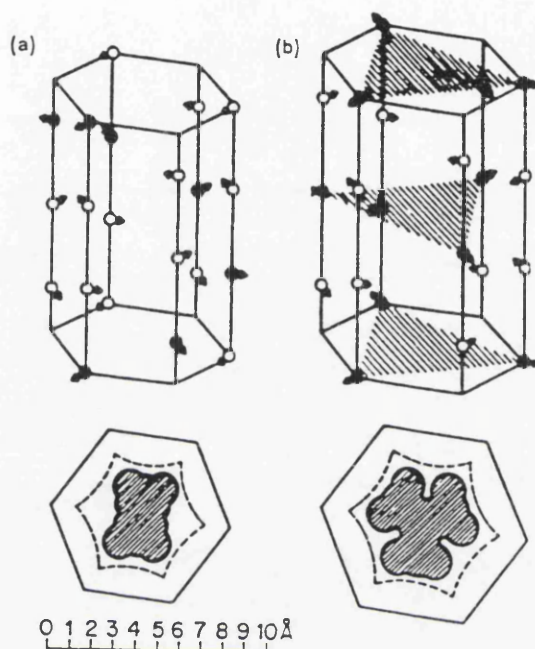
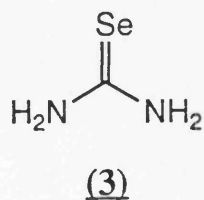


Fig. 8²¹ Fundamental lattices of urea and thiourea inclusion compounds.

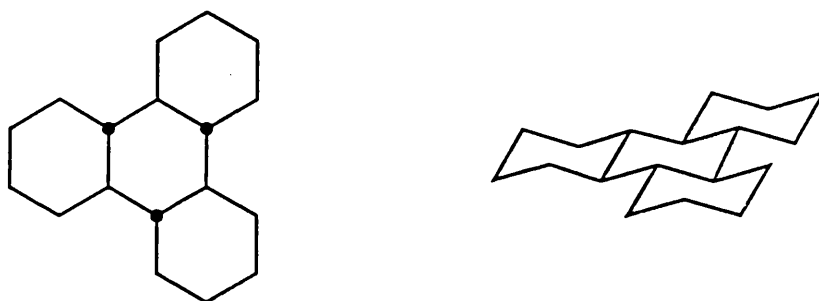
3.1.3 Selenourea

In 1969, Renignse and co-workers²² synthesised selenourea (3) and showed that this too is an inclusion compound.



This is an example of a 2nd Generation host with selenourea being the analogue of urea. Selenourea forms inclusion compounds with a variety of hydrocarbons all of which can also be included in thiourea. Although the difference in channel diameter between thiourea and selenourea inclusion compounds, therefore, appears to be small, selenourea seems to be much more selective. For example, *trans*-1-*tert*-butyl-4-neopentylcyclohexane forms an inclusion compound with selenourea, whereas the *cis* isomer is not included. Thiourea shows no preference in this case.

3.2 Perhydrotriphenylene (PHTP)²³



(4)

trans,anti,trans,anti,trans-Perhydrotriphenylene (4) was found, by chance, to form inclusion compounds by Farina in 1963²⁴. This, therefore, is another example of a 1st Generation host. Many aspects of the solid state behaviour of PHTP are linked to its high degree of molecular symmetry, its rigidity and its inability to exercise strong intramolecular interactions because of its hydrocarbon nature (See Section 2.2). This makes PHTP a true clathrate (Type I). As PHTP possesses D_3 symmetry, the host can exist in two enantiomeric forms, however, it should be noted that (-) PHTP inclusion compounds are

essentially identical to that of (\pm) PHTP. The only significant difference being the space group $P6_3/m$ for the racemic compound and $P6_3$ for the optically active one, because of the absence of the mirror plane. We will only consider (\pm) PHTP inclusion compounds.

There are three main types of crystal structures adopted by inclusion compounds of PHTP, depending on the nature of the guest (this shows how the guest can alter the overall crystal structure of the host to achieve maximum complementarity).

For linear compounds, such as long chain hydrocarbons, fatty acids etc. PHTP crystallises in the $P6_3/m$ space group, as can be seen from the crystal structure of *n*-heptane²⁴ (Fig. 9).

The host structure is comprised of stacks of superimposed PHTP molecules arranged in the hexagonal unit cell. At the vertices of the cell there are channel type cavities, the diameter of which is about 5Å. The guest molecules in these channels are not arranged in fixed positions. To accommodate slightly bulkier guests, e.g. 2,4,4-trimethylpentane the host lattice simply expands by 0.3Å along the *a* and *b* axes of the crystal cell^{25,26}.

Spherical or quasi-spherical molecules, e.g. CCl₄, CHCl₃ etc.²⁵ give rise to a crystal cell of quite different dimensions, with a cell volume typically three times that of the linear adduct. The host lattice, however, closely resembles that of the *n*-heptane adduct. The host-guest ratio is exactly 6:3, yet the guest molecules do not occupy equivalent sites in the cell: two of them are located on the three-fold axes and one on the six-fold hexagonal axis at the vertex of

the unit cell. The chloroform molecules along this axis are rotated by 60° and follow each other statistically in such a way as to simulate hexagonal symmetry. In this inclusion compound there are therefore two different types of channel with different symmetries and dimensions (Fig. 10).

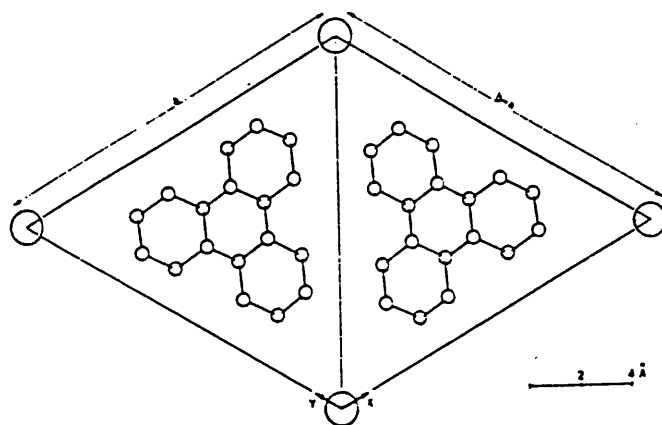


Fig. 9 x - y projection of the crystal cell of the inclusion compound PHTP:*n*-heptane.

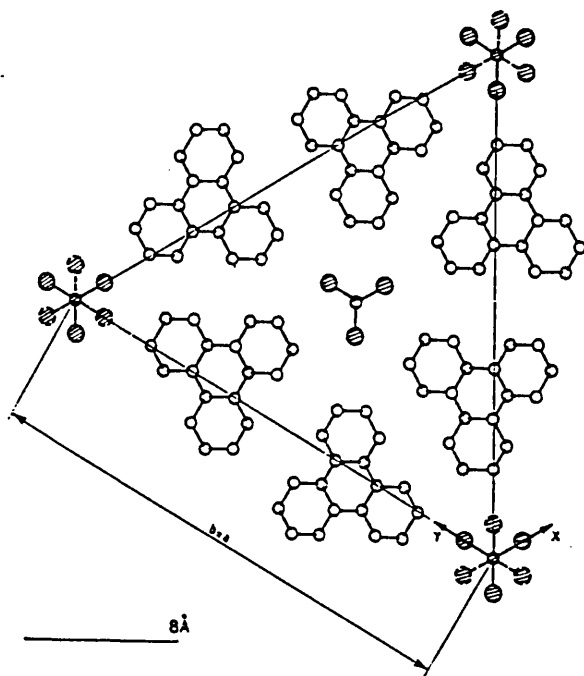


Fig. 10 x-y projection of a part of the crystal cell of the inclusion compound PHTP:chloroform showing the different symmetry of the two channels.

A third kind of structure is found in the inclusion compounds of 1,4-dioxane and cyclohexane. The adduct crystallises in the $R\bar{3}$ space group. The dimensions of a and b are close to those of the inclusion compound with CHCl_3 , whilst the c axis is exactly 9 times greater.

The cell of the PHTP-cyclohexane adduct (Fig. 11) shows PHTP molecules stacked in a slightly displaced manner on the horizontal plane, in such a way that their centre of gravity describes 9/1 helix with a 0.4\AA radius around the ternary crystallographic axis. In addition to its 54 PHTP molecules,

the cell contains 21 cyclohexane molecules in three equivalent channels, properly interlinked with PHTP molecules and statistically arranged in many orientations.

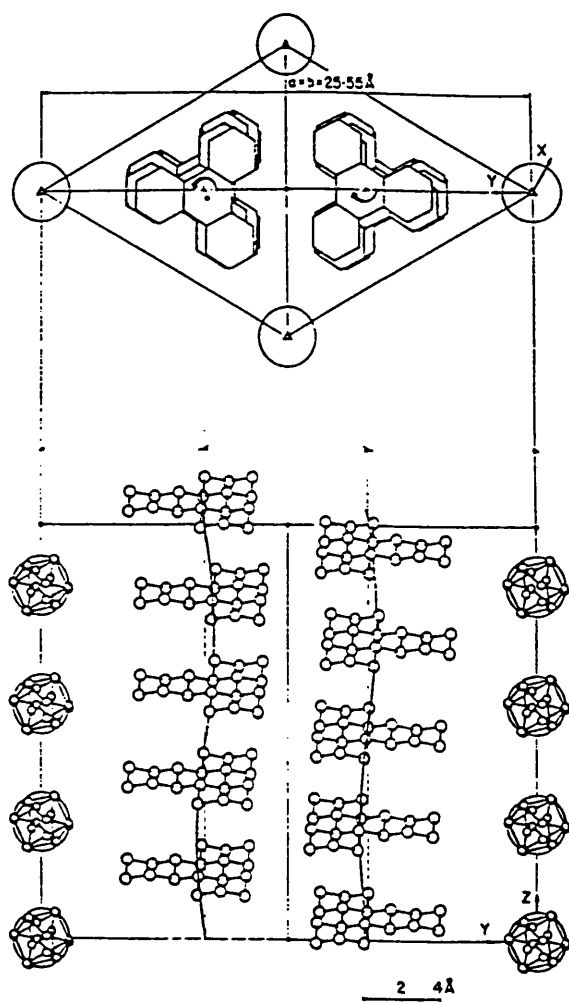
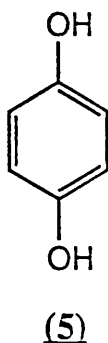


Fig. 11 Top and front view of the crystal cell of the inclusion compound
PHTP:cyclohexane.

3.3 Phenols¹²

3.3.1 Hydroquinone (5)



This is another 1st Generation host and was first discovered as the H_2S clathrate, in 1849, by Wöhler²⁷, but it was not until the 1940's, that the complex structure behind such a simple clathrate was revealed by Powell's X-ray study²⁸.

Further X-ray studies demonstrated that hydroquinone can crystallise in three crystal forms α, β and γ ²⁸⁻³². Only α and β forms include and so are considered here.

The stable α form crystallises in the $R\bar{3}$ space group with 54 molecules of hydroquinone in the hexagonal unit cell, and three crystallographically independent hydroquinone molecules in the asymmetric unit, two are involved in forming two interpenetrating open, hydrogen bonded cages which are capable of clathrating small molecules^{31,34,25}, whereas the third forms double helices consisting of hydrogen bonded chains of molecules round the threefold

screw axes, one of which is denoted by a continuous line at the left side of Fig.

12. This makes α hydroquinone a Type II clathrate.

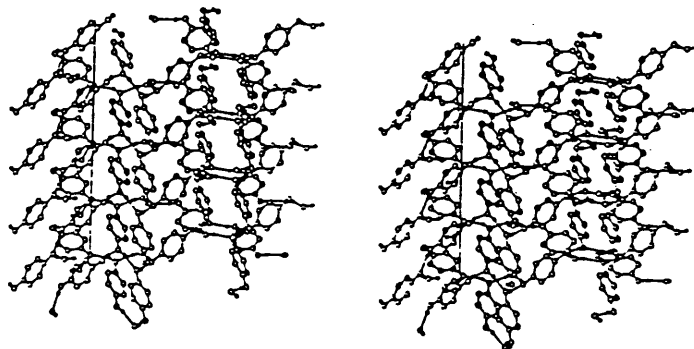


Fig 12. Stereoview illustrating the structure of α -hydroquinone.

The local density for the helical region is high for an organic structure and confirms that this part of the structure cannot include guest molecules. Thus, there are three cages in the unit cell, similar in size to those of the β -form. However, the minimum ratio expected for a hydroquinone clathrates is 18:1 compared to 3:1 for the β hydroquinone clathrates.

The β -form is a very versatile host and has three crystallographically distinguishable kinds of host lattice, Class 1-3.

The H_2S clathrate corresponds to the Class 1 situation for β -hydroquinone, where cavities having $\bar{3}$ symmetry are present (Fig. 13).

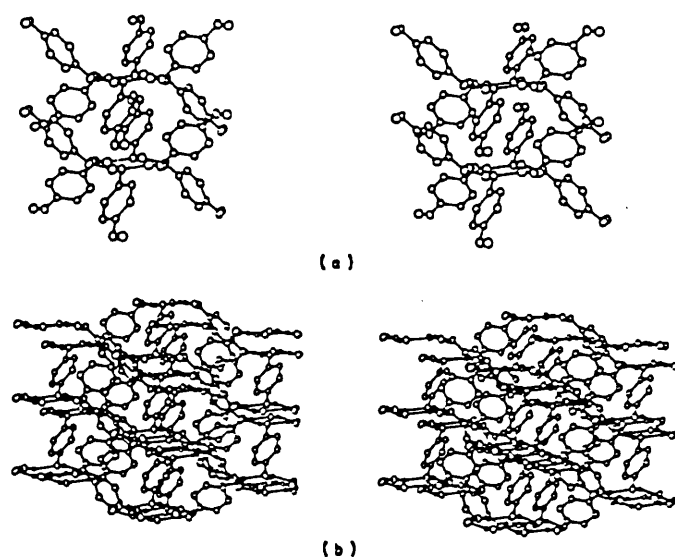


Fig. 13 (a) Stereoview illustrating a single cage of the unsolvated form of β -hydroquinone host lattice (b) interpenetrating networks of β -hydroquinone.

As can be seen, the top and bottom of the void are formed by hexagons of hydrogen bonded oxygen atoms, an ordered arrangement of hydrogen atoms is apparent in the $[\text{OH}]_6$ rings and the host molecules point alternately above and below the mean plane of the (nearly planar) six oxygen atoms. The hexameric units belong to two identical, but displaced, three dimensional interlocking networks. This is a Type II clathrate (coordination assisted clathrate host lattice).

In Class 2 β -hydroquinone clathrate, such as those formed with SO_2 , MeOH and CH_3NC , a lowering of the space group from $R\bar{3}$ to $R3$ is found. The

X-ray of the methanol clathrate³⁶ gives a clue as to why the symmetry drops to *R*3. This is because the hydroxyl group in the methanol interacts with three phenolic oxygen atoms of the adjacent [OH]₆ ring (Fig. 14). This is now a Type IV clathrate.

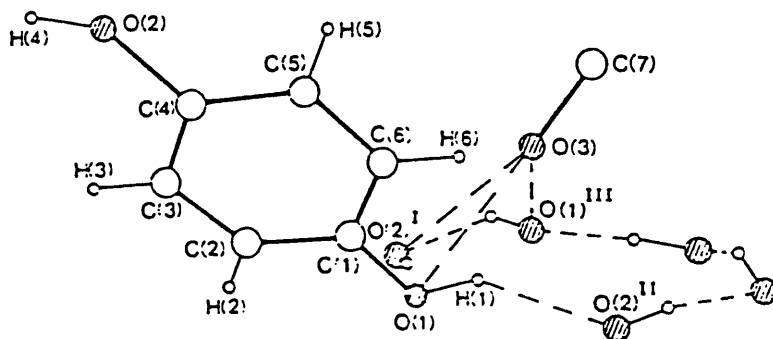


Fig. 14. Host-guest interaction in the methanol clathrate of hydroquinone.

The third class system involves a further lowering of symmetry from *R*3 to *P*3. Only acetonitrile forms this adduct with hydroquinone. It is, again, a Type II clathrate with three symmetry independent acetonitrile molecules fitting snugly inside three distinct cavities³¹.

In 1991, Ermer used this 1st Generation host and produced a 4th Generation clathrate. He reasoned that a single β -hydroquinone network offered a favourable geometry (i.e. shape) for inclusion of buckminster fullerene (C₆₀) as a guest. Furthermore he expected intramolecular interactions in the form of Π - Π interactions.

The $(\text{HQ})_3\text{C}_{60}$ complex³⁷ (Fig. 15) confirmed Ermer's postulate by possessing a single host lattice of hydroquinone enclathrating the C_{60} molecules. Within the complex the C_{60} molecules exhibited orientational disorder. The larger C_{60} molecules have a molecular mass 2.2 times larger than that of the three hydroquinone molecules, and occupy 50% of the crystal volume. Therefore, the $(\text{HQ})_3\text{C}_{60}$ represents one of the rare inclusion compounds with more guest than host material, (in fact it could be argued that C_{60} is the host, see later). This constitutes a fourth class of β -hydroquinone. It is, like class 1 and 3, a Type II clathrate.

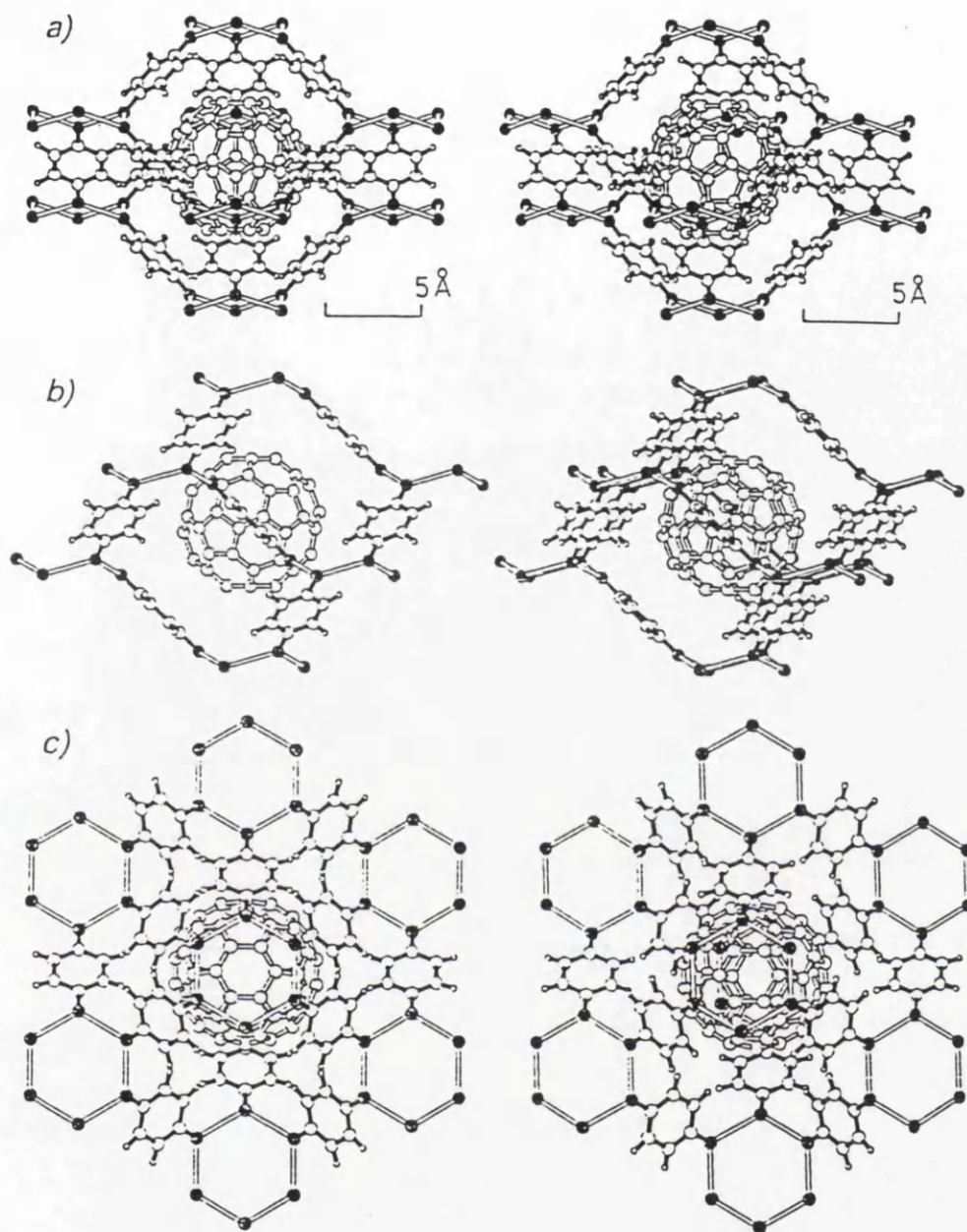
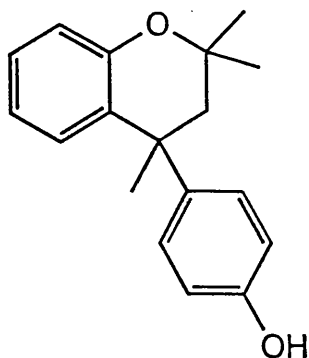


Fig. 15 Ball and stick stereoviews of the super-polonium architecture of $(\text{HQ})_3\text{C}_{60}$. The representation of C_{60} is based on constructed atomic coordinates. The bridging hydrogen atoms of the $(\text{OH})_6$ rings are omitted, and the $\text{O}(\text{H})\text{O}$ bridges are drawn as white bonds; note the pronounced chair-like puckering of the $(\text{OH})_6$ rings.

3.3.2 Dianin's Compound (6)



(6)

A host molecule bearing a close resemblance to β -hydroquinone, at least in the hexameric hydrogen bonded host unit is 4-*p*-hydroxyphenyl-2,2,4-trimethylchroman (6), first prepared by a Russian chemist A.P. Dianin in 1914³⁸.

Its propensity for inclusion was soon realised, forming adducts with guests as diverse as argon^{39,40}, sulphur dioxide⁴⁰, decalin⁴¹ and sulphur hexafluoride⁴².

Most adducts crystallise in the $R\bar{3}$ space group with a host guest ratio of 6:1 and the matrix is held together by hydrogen bonded hexamers (Fig. 16). This again is a Type II clathrate.

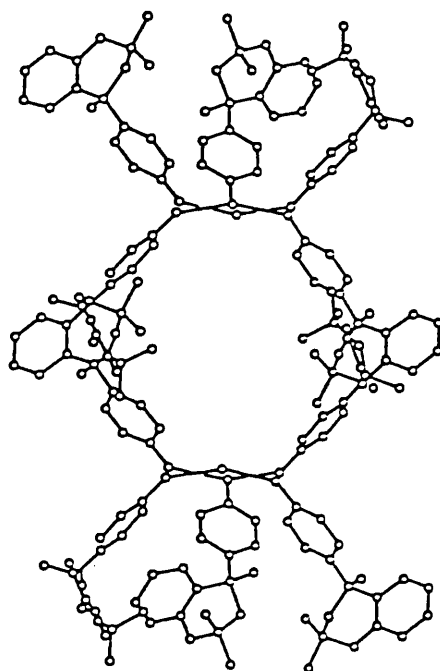


Fig. 16. Illustration of the unsolvated form of Dianin's compound (6), viewed normal to the *ac*-plane. Two molecules of (6) which lie above and below the cavity as viewed in this direction have been excluded (apart from their hydroxyl oxygen atoms) to show the cage more clearly.

At the top and bottom of each cage there are puckered hexagons of six hydroxyl oxygen atoms, linked by a network of hydrogen bonds, and three molecules of one configuration point up, and three of the opposite configuration point downwards. Each particular column is infinite in content

and runs parallel to the *c*-axis: it is surrounded efficiently by six other identical columns related by three-fold screw axes (parallel to *c*), such that no significant spaces are left between columns. The dove-tailing involved in the lateral packing is illustrated in Fig. 17, the projection is one column fitting neatly into the indentation of its neighbour.

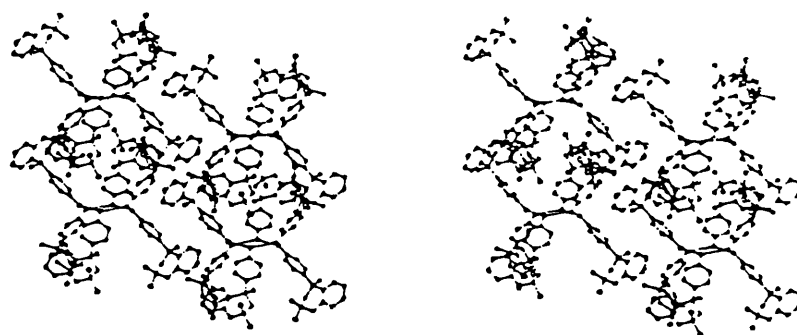
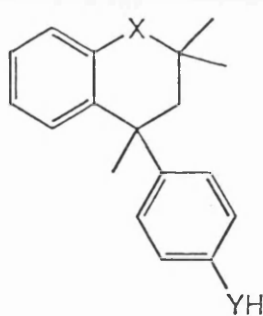


Fig. 17 A stereoview illustrating the dove-tailing involved in the lateral packing of columns, infinitely extended along *c* in unsolvated (6).

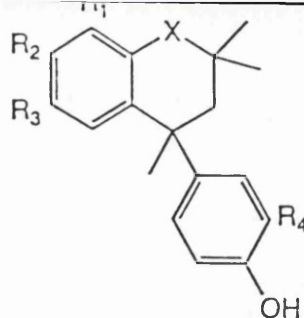
The versatility of Dianin's compound as an inclusion compound first of all prompted Baker⁴¹ to synthesise an analogue (10), which has an additional methyl group *ortho* to the phenolic function however no inclusion ability was observed and it was not until 1969 when MacNicol synthesised the thia-analogue (7)⁴³ did the first inclusion analogue of Dianin's compound appear. This is one of the earliest examples of a 2nd Generation host.

The packing of (7) is, however, almost identical in structure to those of Dianin's compound, and in each guest accommodation is provided in extremely similar hour glass-shaped cavities. This led MacNicol and co-workers to synthesise more derivatives. As can be seen from Fig. 17 the columns comprising the host structure in Dianin's compound are infinite in extent, with any given column surrounded by six identical columns. Since the carbon atoms at C(5), C(6), C(7) and C(8) of the aromatic ring of the chroman or thiachroman are situated on the outside of the columns, it was expected that modification at these positions might interfere with intercolumn packing.

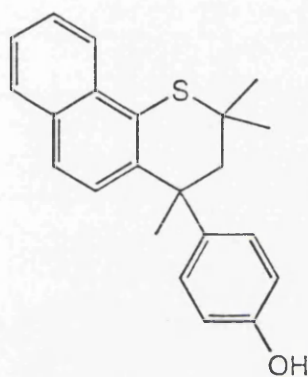
Of these substituted compounds (11)-(17), (11)⁴⁴ (12)⁴⁴, (15)⁴⁵ and (17)⁴⁶ do not form inclusion compounds either due to severe column disruption e.g. (17) or disruption of the hydrogen bonded hexamer in favour of the other hydrogen bonding interactions, e.g. (15). However (13), (14) and (16) do form inclusion compounds and are all isomorphous to (6) and (7), and a fundamental change in cavity size has taken place e.g. in (16), as shown in Fig. 18, the 'legs' of the hexameric unit have 'splayed out', compared with their disposition in (7). The change in cavity shape can be seen from Fig. 19 in which the initial 'hour glass' shaped cavity of (7) has been transformed into the 'chinese-lantern' contour of (14)^{44,47}.



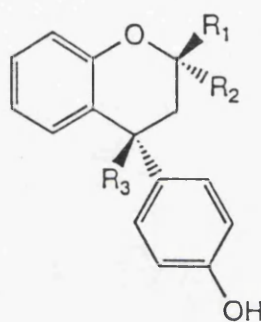
- (6) : X=O, Y=O
 (7) : X=S, Y=O
 (8) : X=O, Y=S
 (9) : X=O, Y=NH



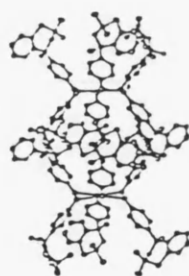
- (10) : R₁=R₂=R₃=H; R₄=Me; X=O
 (11) : R₁=R₂=R₄=H; R₃=Me; X=O
 (12) : R₁=R₃=R₄=H; R₂=Me; X=O
 (13) : R₂=R₃=R₄=H; R₁=Me; X=O
 (14) : R₁=R₂=R₄=H; R₃=Me; X=S
 (15) : R₁=R₃=R₄=H; R₄=Me; X=S
 (16) : R₂=R₃=R₄=H; R₁=Me; X=S



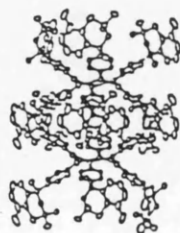
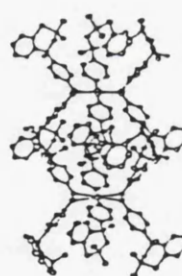
(17)



- (18) : R₂=H; R₁=R₃=Me
 (19) : R₁=H; R₂=R₃=Me
 (20) : R₃=H; R₁=R₂=Me



(a)



(b)

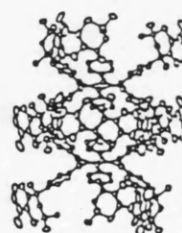


Fig. 18 Comparative stereoviews for (a) the 2,5,5-trimethylhex-3-yn-2-ol clathrate of (7) and (b) the cyclooctane clathrate of (16). The guest molecules are not shown.

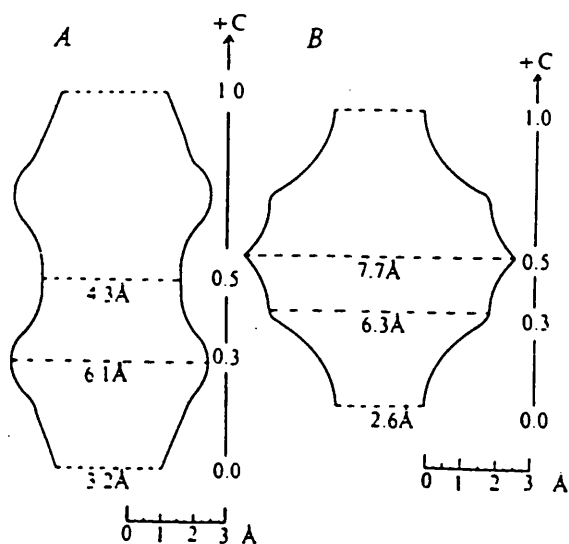


Fig. 19 Section through the van der Waals surface of the cavity for (a) (7) and (b) (16), representing the space available for guest accommodation.

This change in shape is reflected in its clathration properties^{44,46}, for example, on recrystallisation from an equimolar mixture of cyclopentane, cyclohexane, and cycloheptane, (7) greatly favours cyclopentane, whereas (16), with its rounder cavity, favours the larger cyclo-paraffins, this is one of the first times that designing a new host has led to fundamental change in cavity size and, therefore, clathration properties.

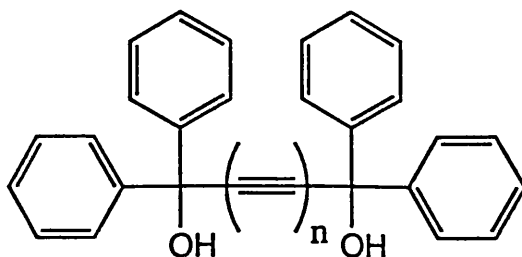
Further changes were sought and removal of one of the methyls at C(2) (18)^{48,49} and (19)⁵⁰ also led to new inclusion compounds, however, removal of the C(4) methyl (20)⁴⁹ destroyed inclusion behaviour. Finally, changing the nature of the hydrogen bonds was explored. The thiol analogue (8) was prepared^{51,52}, and showed inclusion compounds with CCl₄, with an increased c-spacing in keeping with the longer C-S bond, but the amine shows no inclusion ability.

Not only is this a method of designing new hosts but it can help to understand some of the aspects in the molecule that helps it crystallise in an open structure.

3.4 'Wheel and Axle' Hosts

This area started when Toda found, by chance, that the acetylenic diols (21) and (22) formed inclusion compounds⁵³.

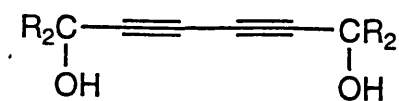
These 1st Generation hosts have two main features. The first is the ability to hydrogen bond and the second is the elongated shape with bulky groups on each of the terminal sp³ carbons.



(21) : n=1

(22) : n=2

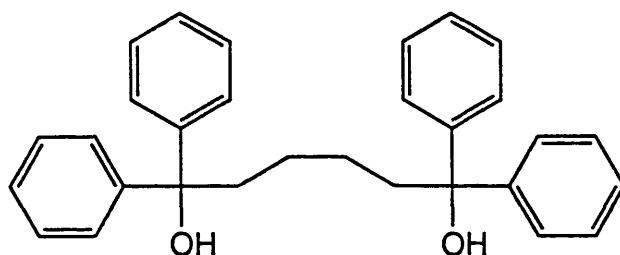
(23) : n=0



(24) : R=Me

(25) : R=Et

The bulky nature of the end groups play an important role in its inclusion properties as can be seen from the fact that the tetra methyl (24)⁵³ and the tetra ethyl (25)⁵⁴ compounds show no inclusion ability.



(26)

Also important is the rigidity of the host. This is substantiated by the finding that 1,1,6,6-tetraphenylhexane-1,6-diol (26) does not form an inclusion compound⁵⁴.

The X-ray crystal structure of the acetone inclusion compound of (21), Fig. 20, shows that indeed both the phenyl and OH groups play a vital role in the inclusion ability of (21). The OH groups hydrogen bond to the acetone making it a Type III host and the phenyls form the walls of the cavity that is occupied by two acetone molecules.

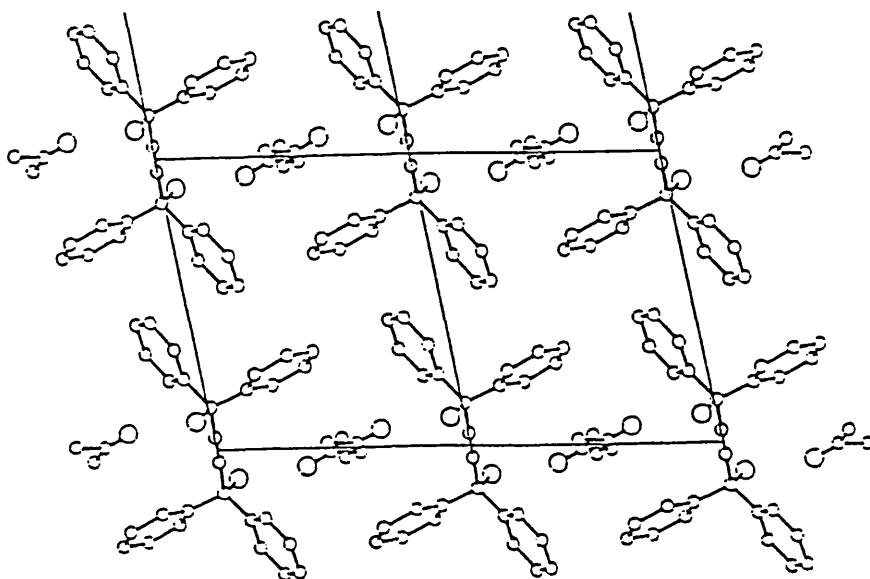
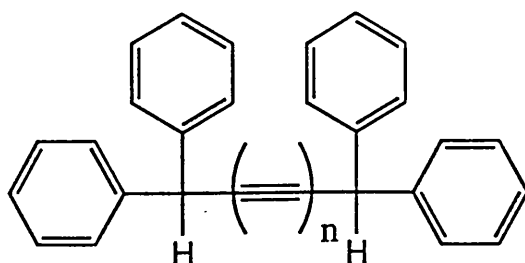


Fig. 20. A packing diagram for the 1:2 complex of (21) with acetone.

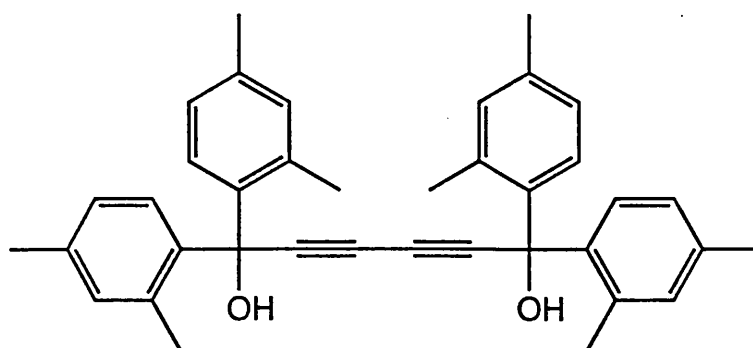
After this Toda then designed some 2nd Generation hosts based on (21) and (22). He found that 1,1,2,2-tetraphenyl-ethane-1,2-diol (23)⁵⁵ includes but this time it forms hosts where hydrogen bonds play no role, and so are Type I clathrates, therefore, he went on to synthesise molecules without the OH moiety (27)-(28)⁵⁵ and he found that they also showed inclusion ability.



(27) : $n=2$

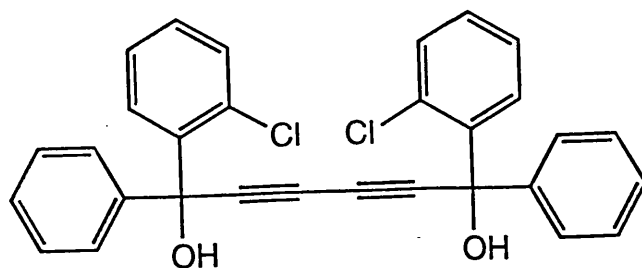
(28) : $n=1$

Toda also found that by changing the aryl groups he could alter the inclusion ability i.e. the larger the group the larger its inclusion ability e.g. (29) shows a high inclusion ability especially for alcohols⁵⁶.



(29)

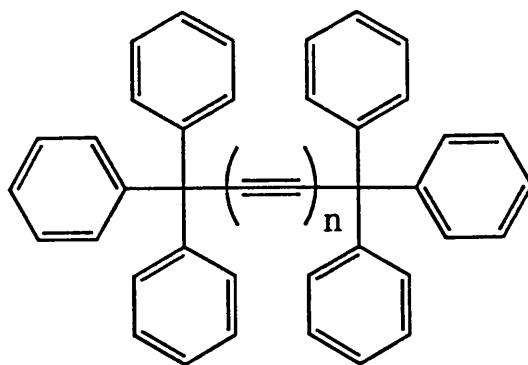
He also synthesised the optically active 1,6-di-(*o*-chlorophenyl)-1,6-diphenylhexa-2,4-diyne-1,6-diol⁵⁷ (30) which has been used for the separation of racemic material and reaction control (see later).



(30)

These hosts were termed 'wheel and axle' inclusion molecules⁵⁸.

In 1984, Hart, realised the importance of the overall shape of the Todas hosts and rationalised that any bulky groups linked by a spacer would have the propensity to include⁵⁹. He first showed this by replacing the OH group with a third aryl group (31) and (32).



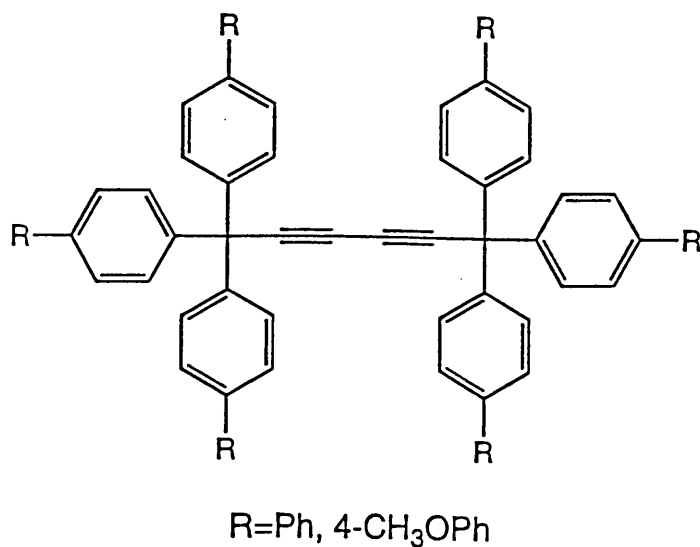
(31) : $n=2$

(32) : $n=3$

This did indeed lead to a new series of Type I clathrates. Although these are 2nd Generation hosts (analogues), because of Hart's realisation of the

importance of overall shape they could be considered as early prototype 4th Generation hosts.

Hart then went on to synthesise a wide variety of hosts based on this principle varying the spacers and aromatic groups e.g. Fig. 21



SPACER : E,E -CH=CH-CH=CH-
 -CH=N-N=CH-
 -(CH₂)₄-
 -(CH₂)₆-
 -CO-CH₂-CH₂-CO-

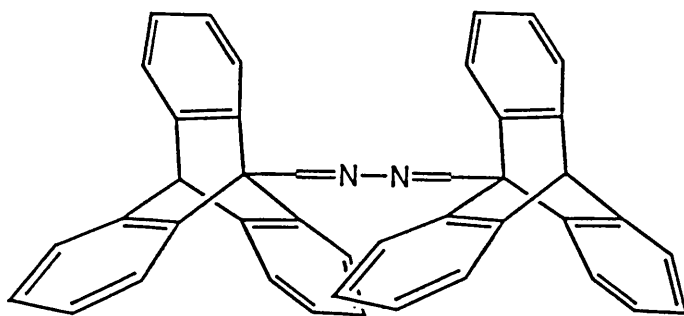
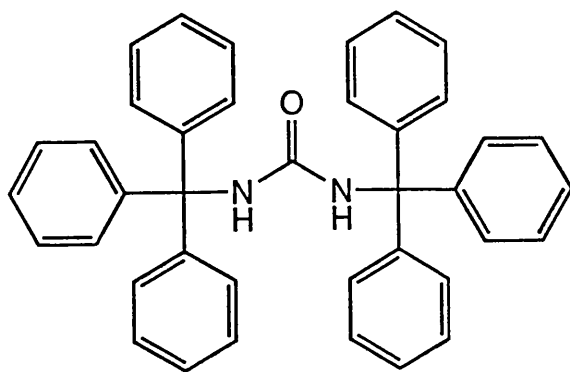


Fig. 21 Some hosts designed by Hart⁵⁹ based on the wheel and axle principle.

Later Goldberg and Hart applied the principle to bulky ureas (33)⁶⁰ which have the added advantage in that they provide a polar region on the central axis allowing it to be involved in intermolecular H-bonding e.g. to a guest.



(33)

Fig. 22 shows the X-ray structure of *N,N'*-ditritylurea (33) with ethyl *N*-acetyl glycinate. It shows the (33) molecule lined up along the *a* axis of the crystal with their urea moieties nearly coplanar. Between the two hosts are guests lined up in an alternating manner. Each guest interacts with two host molecules approaching from opposite sides using hydrogen bonds making it a Type III host.

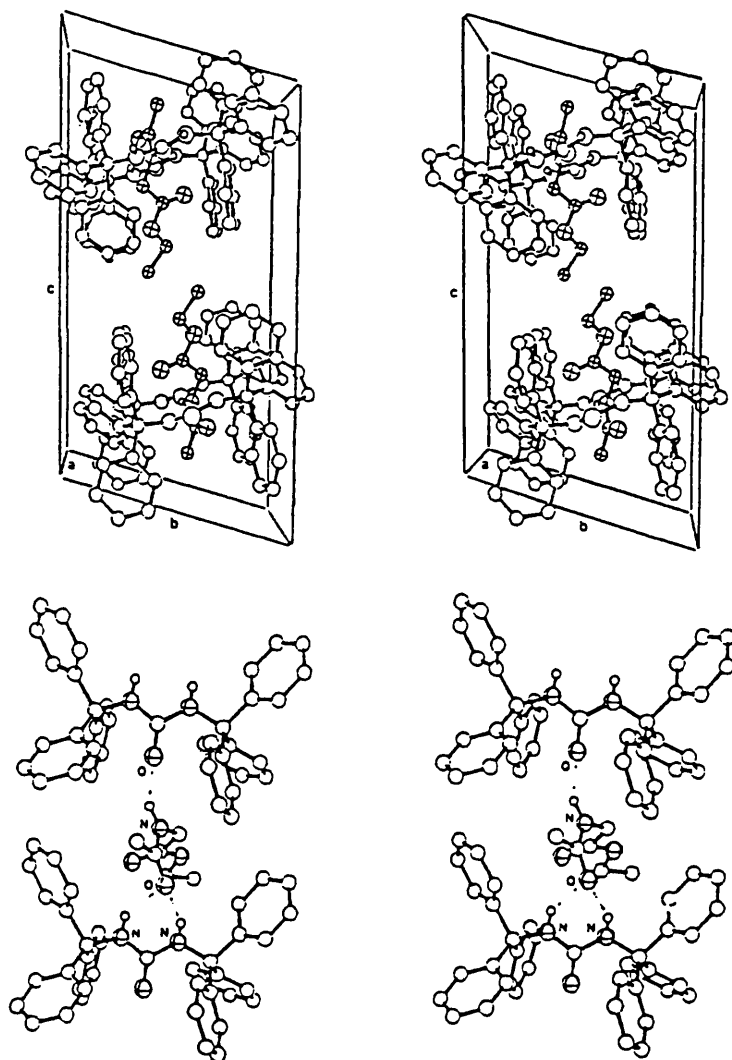
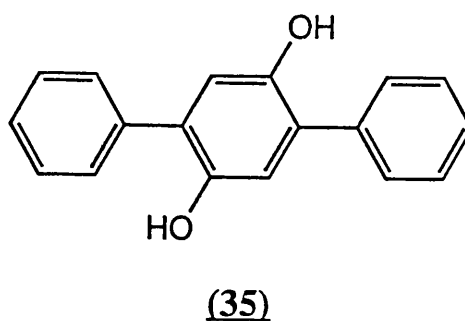
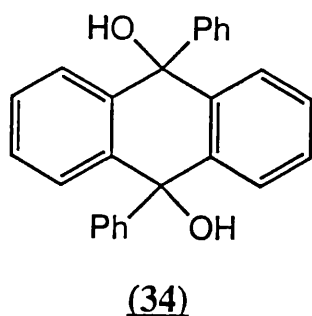


Fig. 22 Stereoviews of (a) the crystal structure of 1:1 (33):ethyl-*N*-acetylglycinate, and (b) the hydrogen-bonding association of the guest to two adjacent hosts related by translation along *a*.

In light of this newly accumulated information on his diol hosts, Toda devised a strategy for the design of new coordinato-clathrates. In essence they must possess the following features (a) some form of diol or dicarboxylic acid functionality capable of participating in hydrogen bonding; this must correspond to an *anti* arrangement. (b) rigidity built into the backbone of the

host molecule to facilitate the formation of a crystalline lattice. (c) a degree of bulk, which should also contribute to a less close-packed host lattice.

Following this strategy Toda chose to examine two molecules for host potential, specifically: 9,10-dihydroxy-9,10-diphenyl-9,10-dihydroanthracene (34) and 2,5-(diphenyl)hydroquinone (35)⁶¹. Both were found to be good hosts.



These truly are 4th Generation hosts, based on intermolecular interactions (hydrogen bonds) rigidity and bulk (shape).

Realising that amides form stable hydrogen-bonded inclusion complexes with his acetylenic diols⁵³, Toda suggested that a diamide should work as a good host molecule for alcohols Fig. 23⁵⁴

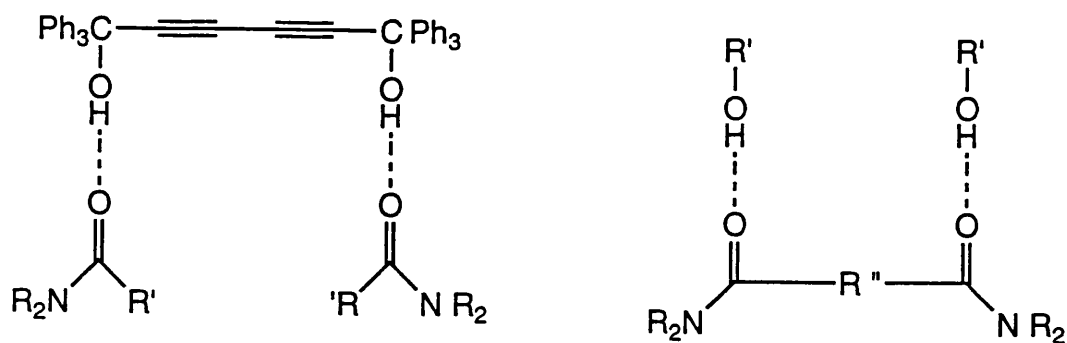
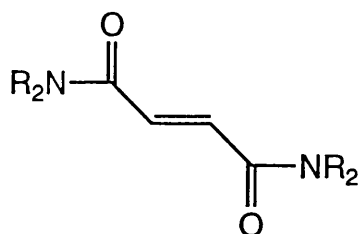
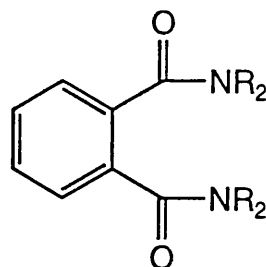


Fig. 23 Toda's analogy for formation of diamine hosts based on his acetylenic diol inclusion compounds with amides.

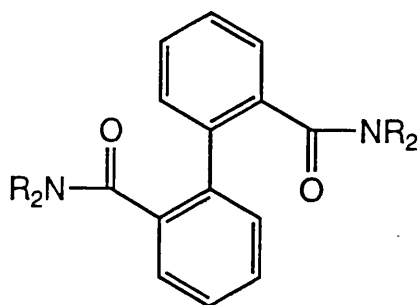
With this in mind he synthesised a variety of diamides and found that they were not only good hosts for alcohols but also capable of forming inclusion compounds with other less polar molecules.



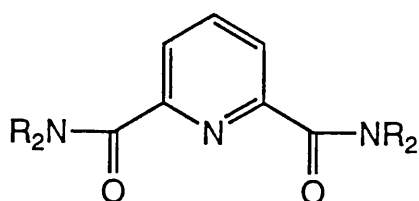
(36)



(37)



(38)



(39)

R = cyclohexyl

For example, *N,N,N',N'*-tetracyclohexyl-1,1'-biphenyl-2,2'-dicarboxamide (38) not only includes alcohols but also includes benzene, CCl_4 and THF. The X-ray (Fig. 24)⁶⁹ of (38) with phenol shows the expected hydrogen bond between host and guest making it a type III host. It is believed that attachment of the phenol molecule to one amide makes the other amide O atom less accessible to a second phenol due to steric reasons.

This strategy is one of pure analogy to the acetylenic alcohols with amide guest making these 3rd Generation hosts.

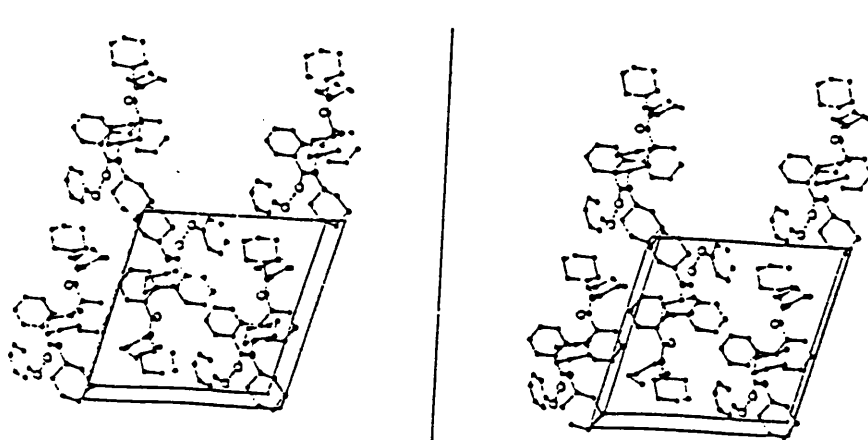
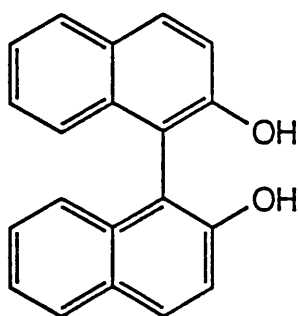


Fig. 24 Stereodrawing of the crystal structure of (38). The origin of the unit cell lies at the upper left corner, with *a* pointing towards the reader, *b* downwards and *c* from left to right. Broken lines represent O-H...O hydrogen bonds.

3.5 Scissor Hosts

After his success with the acetylenic diols and his devised strategy for the design of new coordinato-clathrates, Toda, considered 2,2-dihydroxy-1,1'-binaphthyl (40)⁶².



(40)

Toda's interest in this compound was two-fold.

First it has a large propensity for inclusion⁶³⁻⁷⁰ and second its chiral nature and therefore the possibility of it being used to resolve guest molecules.

Racemic (40) is a good host for amines⁵ mainly due to its ability to form hydrogen bonds as can be seen from Fig. 25. This shows the structure of (40) imidazole (1:2) complex.

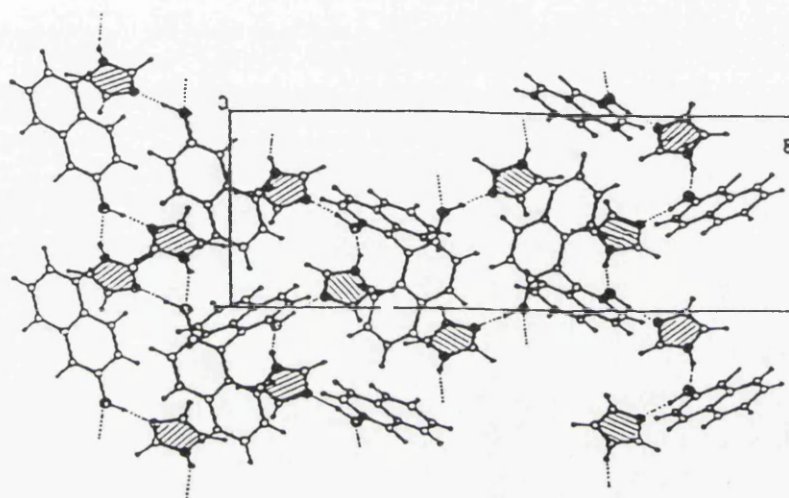
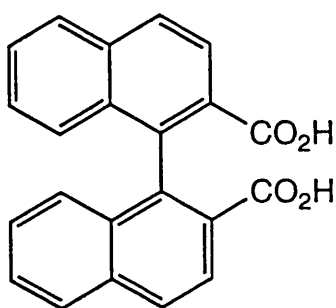


Fig. 25 Crystal structure of the (40) imidazole (1:2) inclusion compound. The imidazole rings are distinguished by hatching.

The host molecule adopts an ideal two-fold symmetry. The imidazole molecules are linked to an infinite spiral with host molecules, as hydrogen bond donor/acceptors complementing the role of the hydroxy functions. The tetragonal crystalline lattice consists of hosts of the same chirality (i.e. spontaneous resolution has occurred) and should be considered as inclusion compounds of the optically resolved host.

Chiral (40) can form inclusion compound with a wide variety of guests that have a hydrogen bond acceptor e.g. sulfoxides,⁷⁰ sulfoximines⁶⁶, phosphinates⁶⁸, etc.

At the same time that Toda had designed (40), Weber by chance discovered that (41) was a host⁷¹.



(41)

He noticed the molecules close resemblance to a pair of tailor's scissors, and subsequently called the molecule a scissor host (Fig. 26).

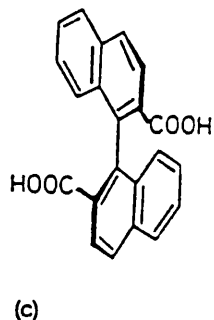
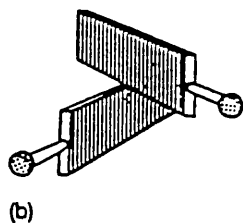
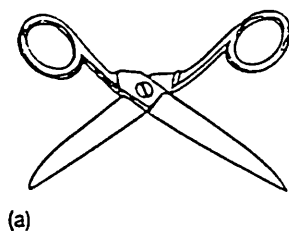


Fig. 26 Scissor Hosts.

Racemic (41) includes a wide variety of guests, mainly alcohols, but also non polar guests. This suggests that (41) forms different types of host structures.

The basic structural pattern which is observed in the crystal packing of the alcohol inclusion compound of racemic (41) is a channel matrix formed by the host⁵. The walls of these channels are regularly interrupted by protruding carboxylic groups, where the polar ends of the guests are located (Fig. 27).

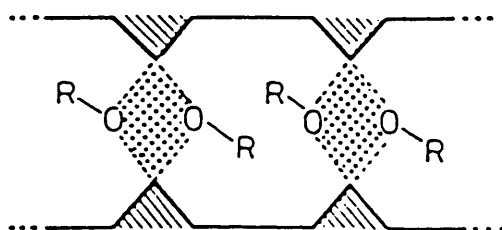


Fig. 27 Longitudinal cross-section of the inclusion channel for the simple alcohol inclusion complexes of (41) (schematic representation); hatched triangles and dotted squares represent polar areas.

The nature of the guest, however, affects the intermolecular bonding in these polar areas and this changes the size and shape of the cavity. Fig. 28 gives a systematic representation of the bonding of different alcoholic guests in these polar regions.

In the methanol clathrate (b), the dimensions of the cleft formed by surrounding groups are 6.5Å height and 5.6Å depth. This is a Type III clathrate. The same type of clathrate is obtained when the guest size is

increased to ethanol or 2-propanol, however, the width of the cage is increased to 6Å with a height of 4Å. With 2-butanol (a) as the guest, the walls of the participating naphthyl moieties are no longer parallel, giving rise to a parallelepiped-shaped cavity. This is a Type IV clathrate. With 1-butanol (c), the clathrate is similar to that formed by ethanol, however, there is one major difference, there are host-host interactions forming host dimers. Finally, the ethylene glycol inclusion compound of (41) forms a hydrophilic cavity intra- rather than inter-molecularly. The guest molecule, which has a relatively small lipophilic surface, fits partly into a preformed void of the host molecule. The result is a non-channel or cavity-type structure which is more compact.

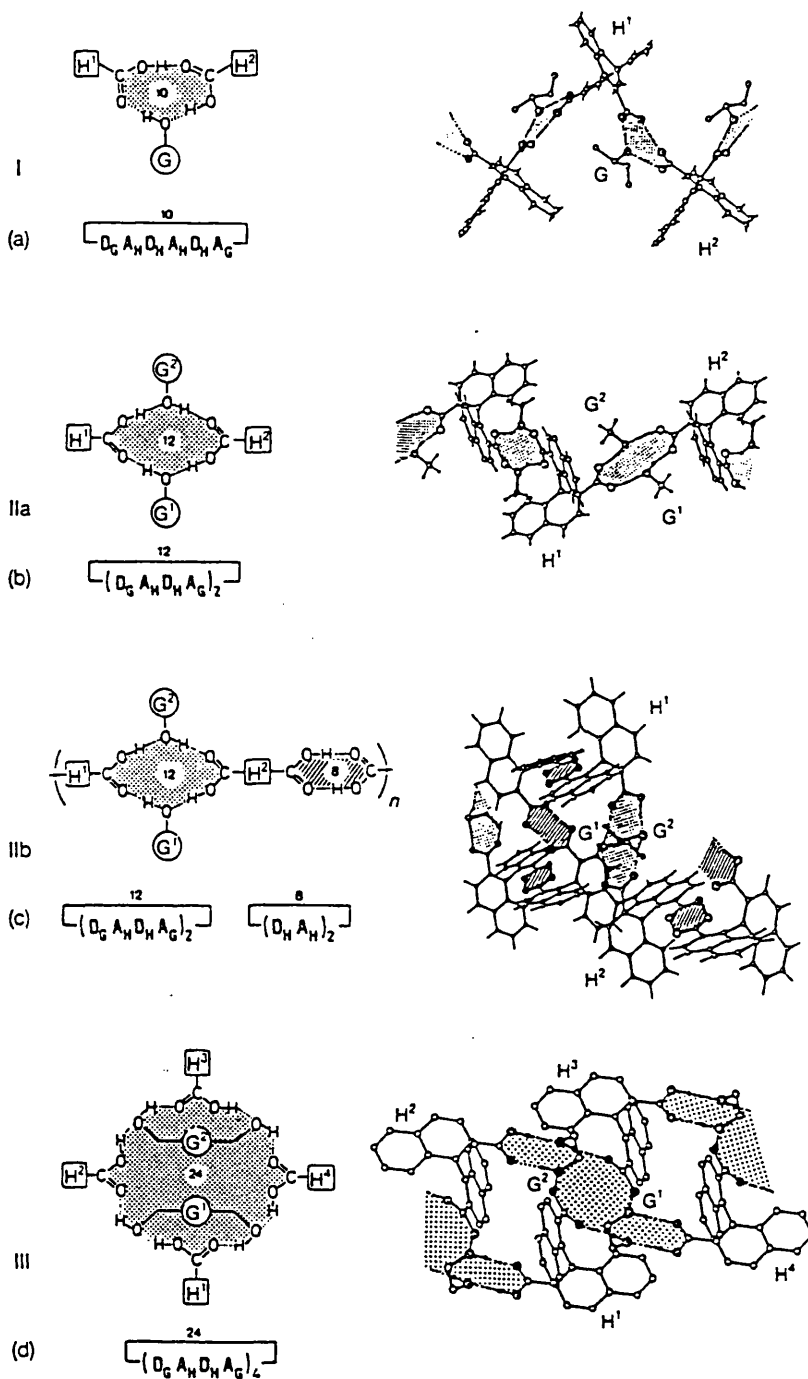


Fig. 28 Principle H-bond interactions found in the alcohol inclusions of (41). Characteristic closed H-bond loops (dotted and hatched regions indicating host-guest and host-host interactions, respectively) and packing examples showing the rings formed in the coordinato-clathrates. Designations used for these: 'H' - host, 'G' - guest, 'A' - acceptor, 'D' - donor. The number in the centre of a H-bond ring indicates the size, inclusive of H atoms. A H-bond is designated as a broken line. O atoms are dotted.

The above study merely reinforces the idea of complementarity (that is, how the host adjusts its packing in order to incorporate the guest). Further evidence of this was obtained by examining the adducts of (41) with acetic acid⁷², DMF⁷³ or DMSO⁷³. Interestingly enough (41) includes bromobenzene⁷³, here there is no chance of host-guest hydrogen bonded interactions and a Type II clathrate is formed with formation of infinite chains of hydrogen-bonded, carboxylic group-dimerised, host molecules of alternating chirality (Fig. 29). Owing to the shape of the host, the chain consists of segments in a zig-zag like arrangement which offers the possibility of having the guest molecules included in the apolar clefts found between these chains. It should also be noted that in line with the above structure that uses both enantiomers in building the host lattice, chiral (41) shows limited inclusion ability⁷⁴.

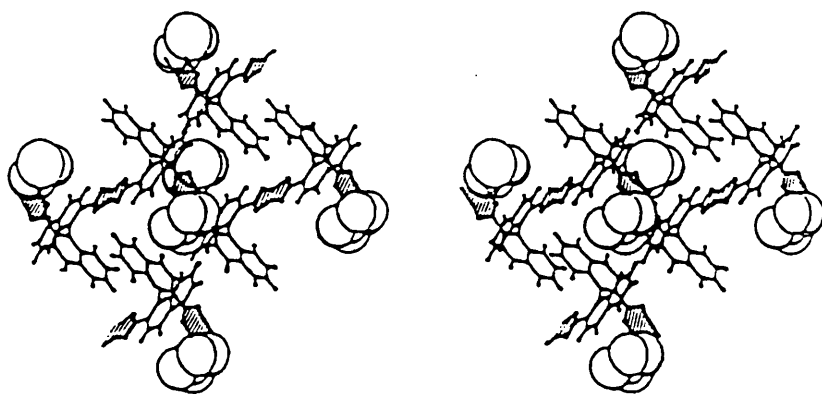


Fig. 29. Crystal structure of (41).bromobenzene (1:1) inclusion compound.

With this inclusion ability in mind, Weber came up with his own theory for designing coordinato clathrates^{75,76} based on two main criteria.

(a) a bulky basic skeleton which makes available the lattice cavities of a clathrate (b) appended functional groups (complementary sensor groups) which govern the coordination to the included guest substrate. Fig. 30 shows this theory diagrammatically and it was from this that Weber went on to produce a series of 2nd Generation hosts based on (41). Fig. 31 shows a list of compounds either with altered skeletons or sensor groups.

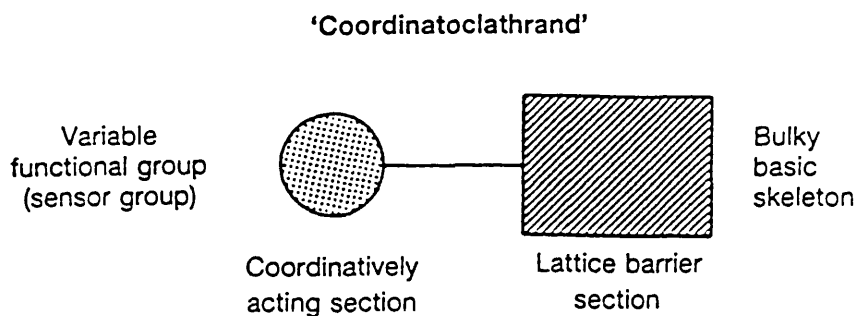
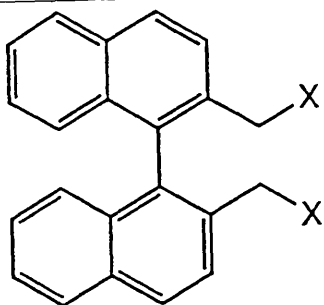


Fig. 30 The Coordinato-clathrand

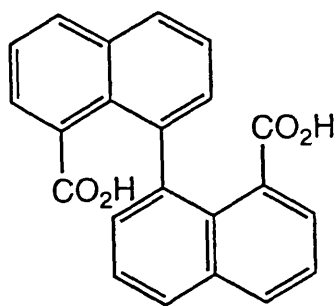
(42) and (43) are obviously homologues of (40) and (41) with an additional methylene group. This, however, introduces more flexibility into the core and so both (42) and (43) do not include⁵. (44) changes, only, the position of the sensor (CO_2H) groups. This also results in complete loss of inclusion ability, however, it does form salt-type associations with pyridine and this salt can then include a variety of molecules⁷⁷. Fig. 32 shows how this salt includes acetic acid. It can be seen from Fig. 32(b) that there is an intramolecular H-bond in the host and the acidic proton of the guest binds to the carboxylic anion. Here

intramolecular bonding works against the net bulkiness of the molecule and helps to explain why (44) itself does not include.

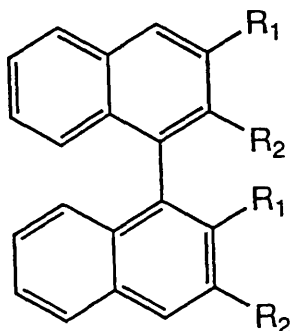


(42) : $X = OH$

(43) : $X = CO_2H$



(44)

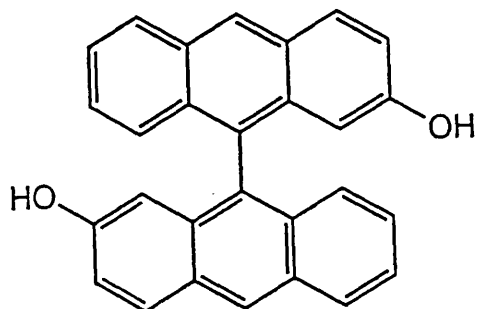


(45) : $R_1 = CO_2H, R_2 = OH$

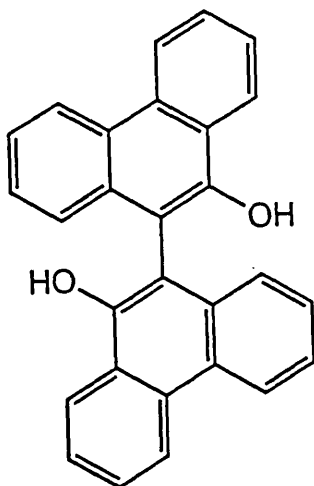
(46) : $R_1 = CO_2H, R_2 = OMe$

(47) : $R_1 = CO_2Me, R_2 = OH$

(48) : $R_1 = CO_2Me, R_2 = OMe$



(49)



(50)

Fig. 31 Other Scissor Molecules.

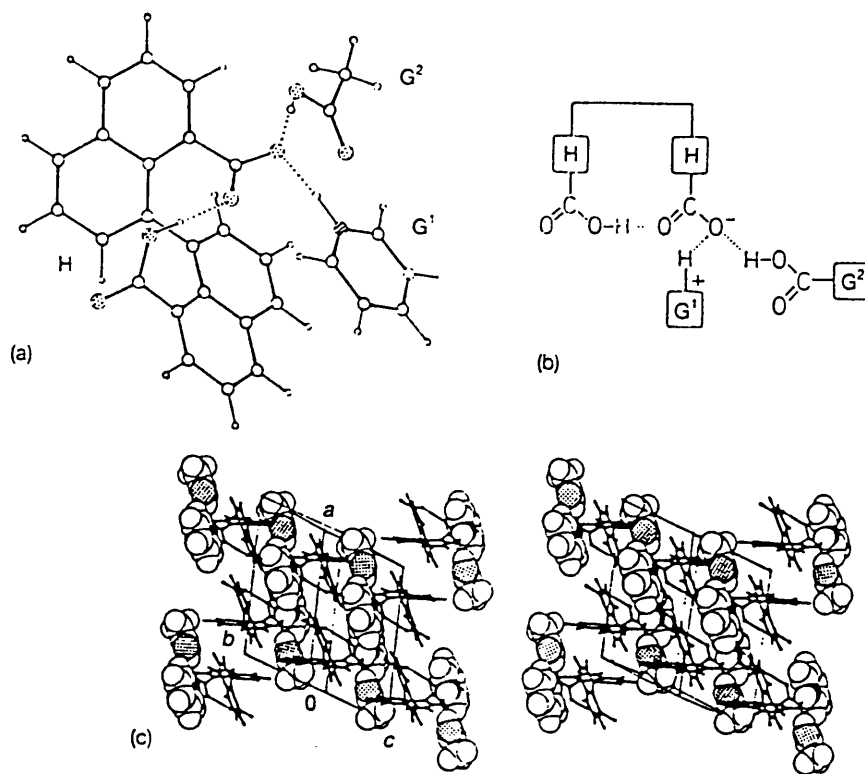


Fig. 32 Crystal structure of the ternary (salt-like) aggregate (42)·pyridine·acetic acid (1:1:1) : (a) molecular structure, (b) scheme of H bonds involved, (c) packing illustration (stereoview). In (c), the 'host molecules' are in a stick style, the 'guest molecules' (pyridine and acetic acid) are in space fitting representation; N atoms specified by black filling, O atoms by shading.

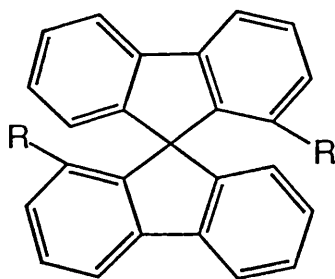
This intramolecular bonding is a problem in (45) and it only has moderate inclusion behaviour⁵. (46) was expected to get round this problem by replacing the hydroxy with a methoxy and therefore removing its propensity for intramolecular bonding. However, (46) does not form coordinato-clathrates but instead forms Type II clathrates with aprotic guest molecules⁵. (47), the diester, does include bromobenzene (1:1)⁷⁸ but this time there is no

intermolecular hydrogen bonding and so it is a Type I clathrate. The hydroxyl group is used in intramolecular hydrogen bonding to the carbonyl oxygen atoms, therefore, introducing more preorganisation into the molecule. (48) has no protonic function left and is ineffective as a host.

(49)⁶³ and (50)⁶⁹ involves changing the bulky group rather than the sensor, this corresponds to structural enlargements of host (40). Both these compounds include a wide variety of guests, mainly of an aprotic type.

Whilst the biaryls are flexible with reference to the central bond, the next step was to increase the preorganisation by removing this flexibility. This can be achieved by spiro-hosts (scissor hosts with a fixed angle).

To test this theory Weber selected four compounds for analysis :



- (51) : R = CO₂H
(52) : R = OH
(53) : R = COMe
(54) : R = CH₂OH

The compounds belong to the same chiral point group as the binaphthylenes C_2 and both racemic and resolved host molecules were examined^{5,79,80}. In general the inclusion behaviour was found in the racemic hosts with the singular exception of (54) which only formed an adduct in the optically pure state.

The molecular architecture of such spiro-type clathrates can be deduced from crystal structures of two inclusion complexes, namely racemic (51). DMF⁸⁰ and (*R*)-(+)-(54). benzene.

Fig. 33 shows the crystal structure of racemic (51).DMF. Here the formamide moiety acts as a hydrogen bond acceptor and donor with a carboxylic group on the host. This corresponds to a Type III host.

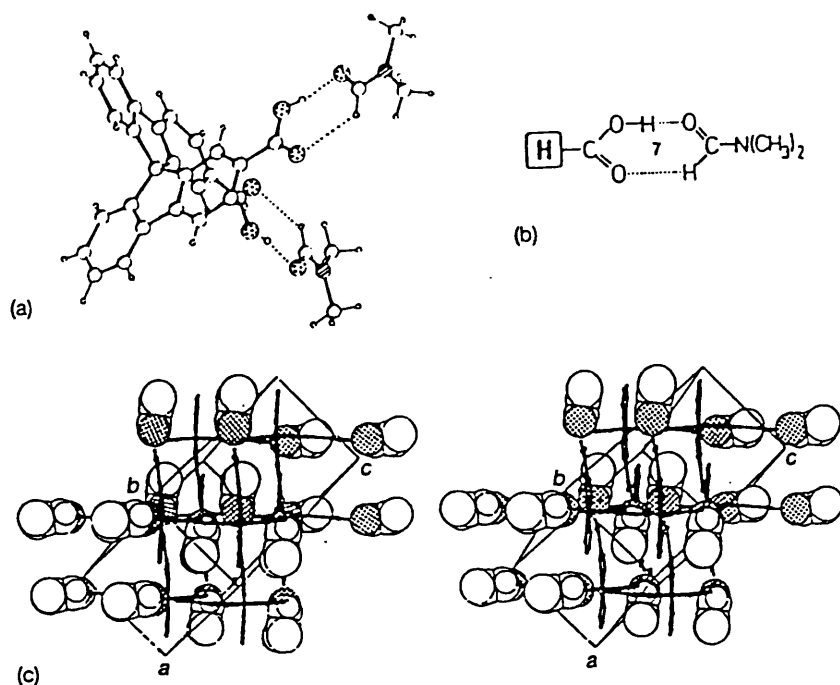


Fig. 33 Crystal structure of (51).DMF (1:2) inclusion compound: (a) molecular structure, (b) scheme of H bonds involved, (c) packing illustration (stereoview). In (c), the host molecules are represented in a stick style, the guest molecules are in a space filling representation.

The structure for (*R*)-(+)-(54).benzene (Fig. 34) is different, however, and corresponds to a Type II clathrate. There is a certain similarity between binaphthyl (Fig. 29) and the spiro molecules here. Both adducts are of Type II and the host molecules in the two adducts are bound into infinite zig-zag chains by hydrogen bonds, the disordered benzene molecules appearing between such chains.

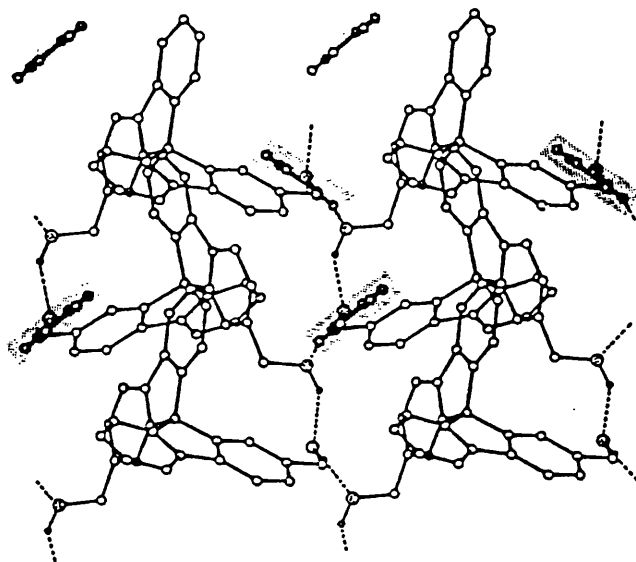


Fig. 34 Crystal structure of (R)-(+)-(54).benzene (1:1) inclusion compound; packing illustration. The guest molecules are indicated by shading.

Further development of the design of the coordinato-clathrate can be seen in Weber's roof-shaped hosts^{75, 81} (Fig. 35).

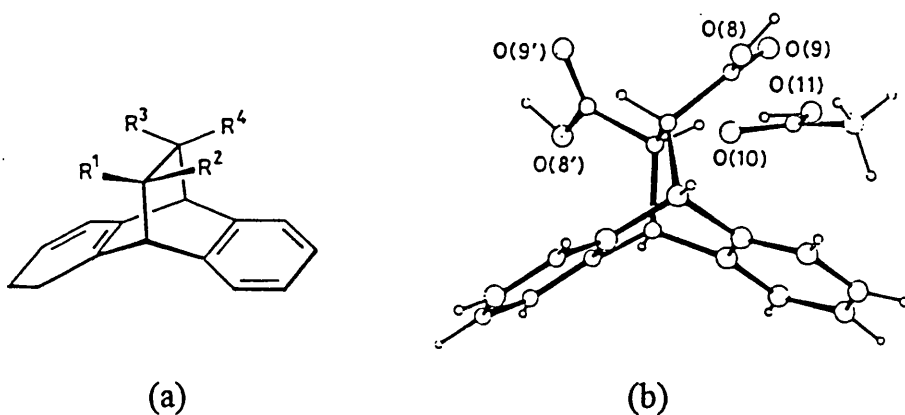


Fig. 35 Webers roof-shaped hosts (a) General structure
(b) Perspective view of *trans*-9,10-dihydro-9,10-ethanoanthracene-11,12-dicarboxylic acid : acetic acid clathrate

These type of molecules also have the rigid molecular skeleton and sensor group.

Although the sensor group is vital for the formation of coordinato-clathrates, following the same principle of Toda and Hart of removal of functional groups in the 'wheel and axle' hosts (see 3.4), Toda and Weber discovered a new set of Type I clathrates.

Compounds (55a, b), (56) and (57a-d) all form inclusion compounds⁵. The packing of the non-polar scissor host molecules is illustrated by the crystalline inclusion compound between (56) and benzene (Fig. 36)⁸².

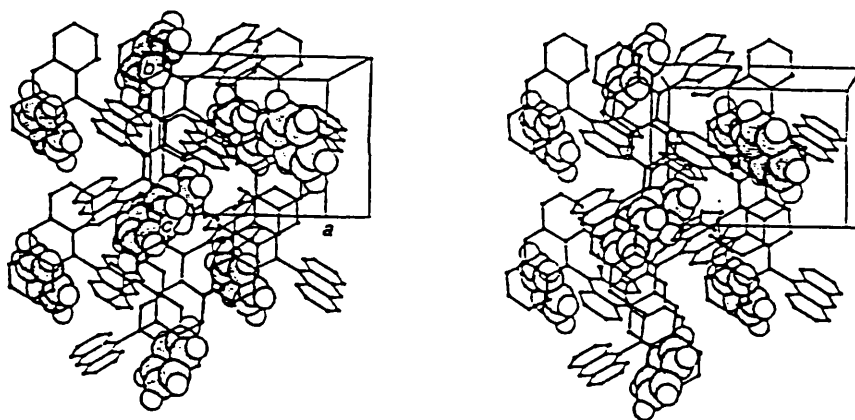
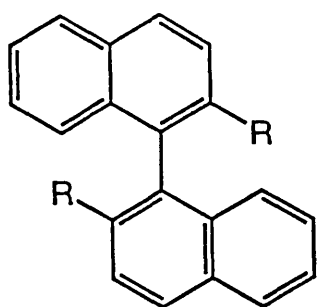
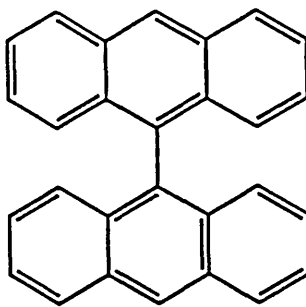


Fig. 36. Crystal structure of the (56).benzene (1:1) inclusion compound: Stereoscopic packing illustration. The host molecules are represented in a stick style, the guest molecules are in a space filling representation.

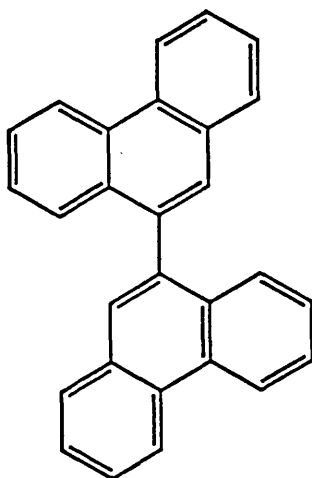
The guest molecule is perfectly ordered within the crystal. This is explained by the tight fit of the pair of benzene guests occupying almost



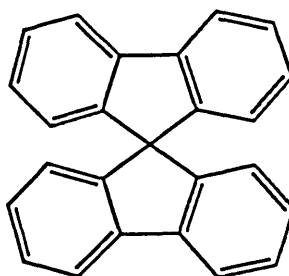
(55a) : R = H
 (55b) : R = Me



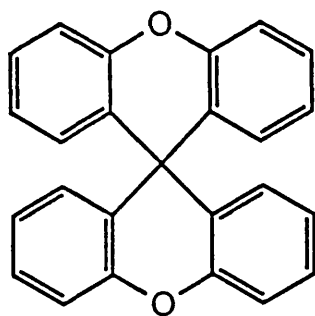
(56)



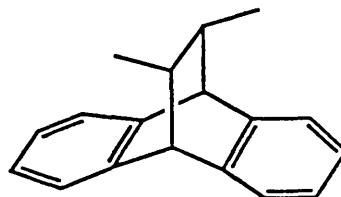
(57a)



(57b)



(57c)



(57d)

completely closed cages which are formed by the flat surfaces from eight contributing host molecules.

The work by Toda, Weber and Hart on the 'wheel and axle' and scissor hosts demonstrates a very logical approach to design, introducing new hosts to the series based on previous experimental observations. This was highlighted by Toda's discovery of non-functionalised scissor host molecules.

The work also provided valuable information in host structure, important features being bulk and rigidity but also how intermolecular bonding can force a host into different clathrate structures or even bind to a guest. It also introduced the idea of molecular symmetry, although they did not use this in their overall design strategy, as most of their molecules possess C_2 symmetry.

3.6 Hexa-hosts and Symmetry

3.6.1 The Hexa-hosts

Up until the mid-1970's all hosts had been discovered by chance (1st Generation) and then altered to develop new hosts (2nd Generation). It was then that the first purely designed host was synthesised, by MacNicol⁸³. The concept (Fig. 37) was essentially derived from the packing modes of such classical hosts as hydroquinone, phenol and especially, Dianin's compound (See Section 3.3).

MacNicol noticed the parallel between the hydrogen bonded hexamer, (A) which maintains the open structure, that is of a temporary nature and the structure of a suitably hexasubstituted benzene (B), and reasoned that molecules of the latter might possess a greatly increased tendency to crystallise forming non-close packed structures with inclusion properties.

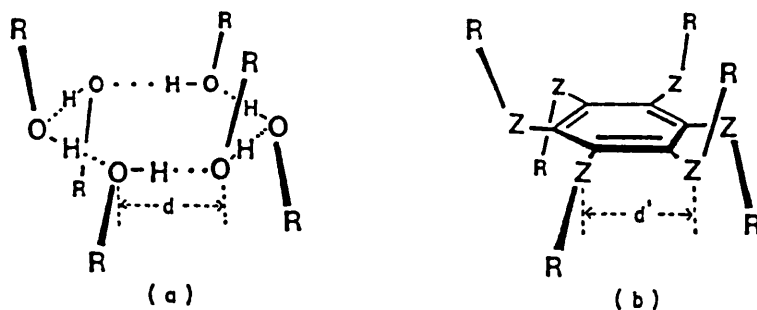
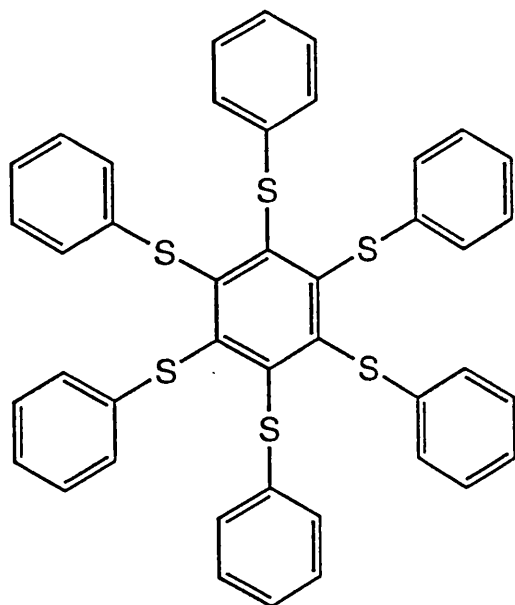


Fig. 37 Comparison of (a) hydrogen bonded hexamer unit with (b) hexasubstituted benzene analogue.

MacNicol also noted the favourable correspondence of the overall geometric aspects and the hexamer dimensions of unit (A) and (B). In doing so he introduced design by analogy (3rd Generation hosts). Preorganisation, again, is apparent here, replacement of the temporary hydrogen bonded hexamer with a permanent benzene ring.

The strategy involved synthesising a series of such hosts, termed the hexa-hosts, by substituting hexahalobenzenes with various phenolate, thiophenolate or selenophenolate nucleophiles. The first hexa-host synthesised was hexakis(phenylthio)benzene (58).



(58)

This was found to include CCl_4 , CCl_3CH_3 and other chlorine molecules⁸³. The inclusion compound crystallises in the $R\bar{3}$ space group with three host molecules and six guest in the hexagonal unit cell. The packing diagram (Fig. 38) shows that the adduct is a Type I clathrate ('true' clathrate). The host molecules completely encapsulates the guest molecules in a cage by van der Waals interactions.

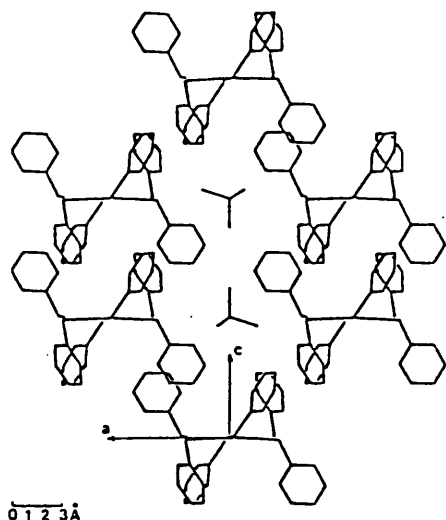


Fig.38 An illustration of the host-guest packing in the crystal of the CCl_4 clathrate of (58), as viewed onto the ac plane. Two host molecules which lie above and below the cavity as viewed in this direction have been excluded.

To prove this was no isolated discovery of a host compound MacNicol extended the series, but due to synthetic difficulties the series investigated was the two atom linked hexa-hosts⁸³. This involved substituting hexakis (bromomethyl)benzene, $\text{C}_6(\text{CH}_2\text{Br})_6$, with the aforementioned nucleophiles as well as nitrogen-based nucleophiles, Fig. 39 shows the general structure of these new molecules.

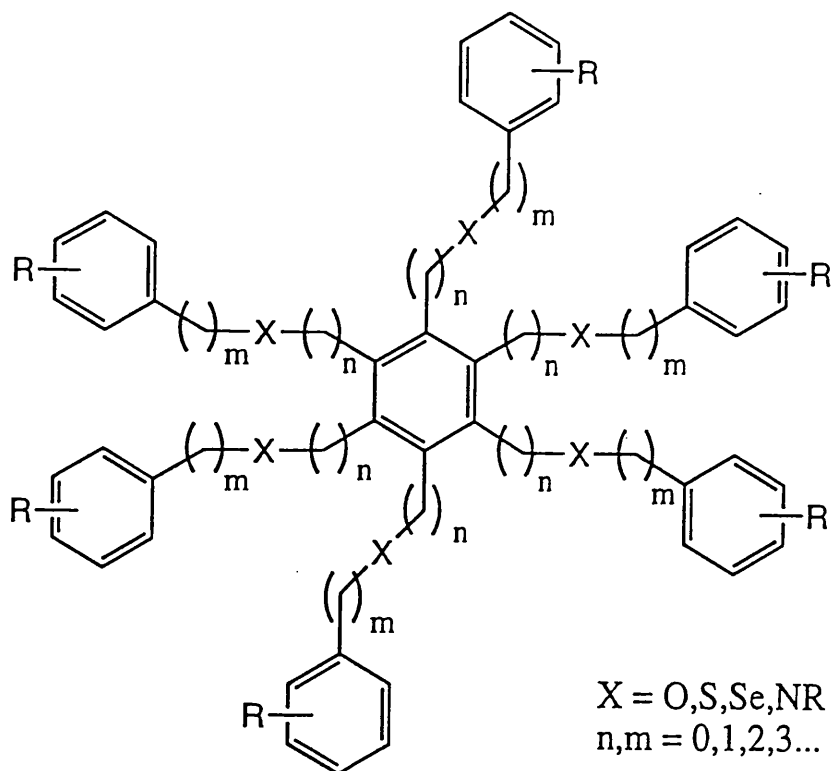
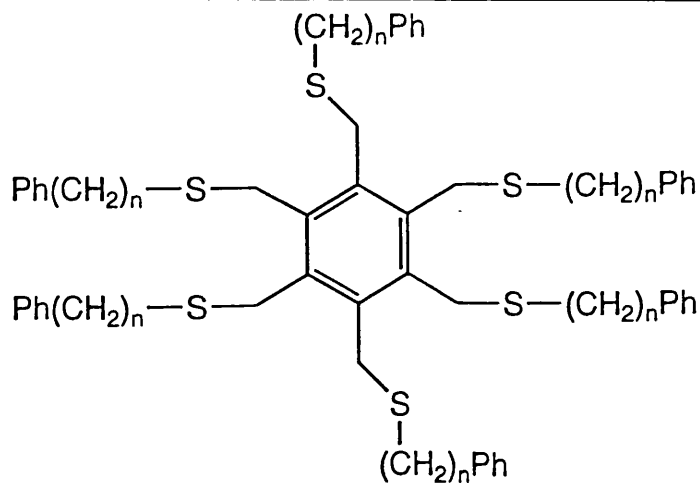


Fig. 39 General Hexa-Host Structure.

This led to a study⁸⁴ of chain elongation in the legs. (59)-(62) shows a series of molecules with their only difference being in the number of CH₂ moieties in the chain. (59)-(61) all show inclusion behaviour, (62) on the other hand does not. This is thought to be due to two factors (1) less rigidity in the molecule due to the extended chains and (2) as the legs are extended there is a greater deviation from the three-fold symmetry⁸⁵.



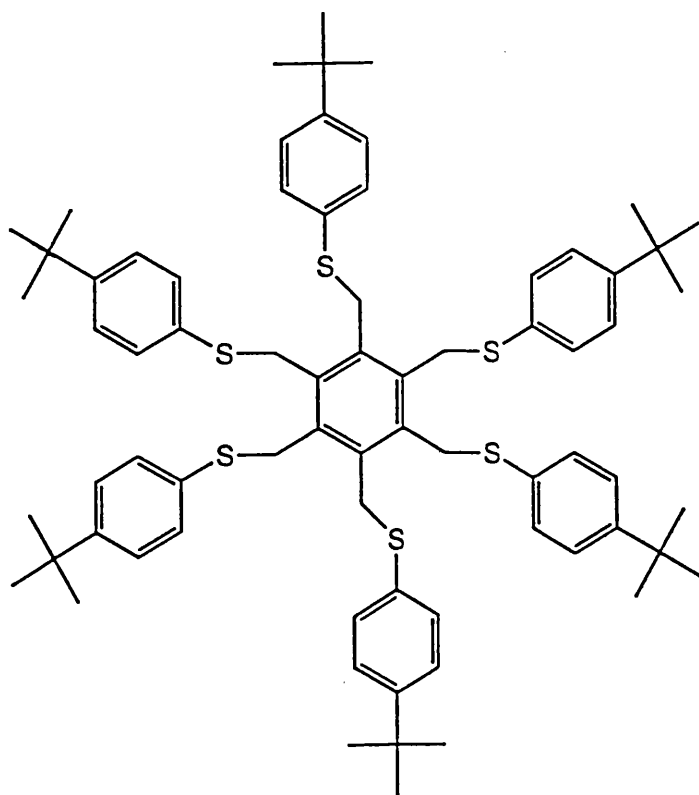
(59) : $n=0$

(60) : $n=1$

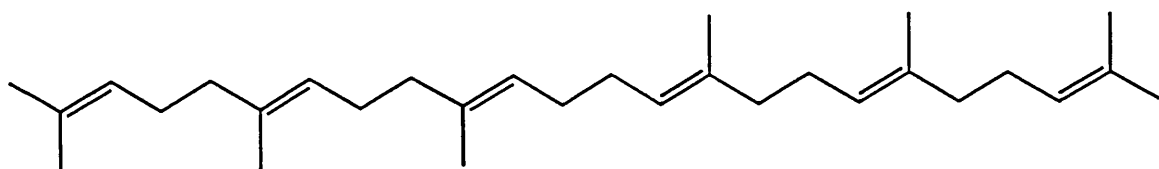
(61) : $n=2$

(62) : $n=3$

The nature of the analogy means that the cavity in the inclusion compounds should be a cage. There is one, however, that has channel type cavities. Hexakis(*p*-*t*-butylphenylthiomethyl)benzene (63) includes a variety of guests including the large triterpene, squalene⁸⁶ $\text{C}_{30}\text{H}_{50}$ (64). As can be seen from Fig. 40 the squalene is located in the channel, as a pair of enantiomeric conformations belonging to the point group C_1 .



(63)



(64)

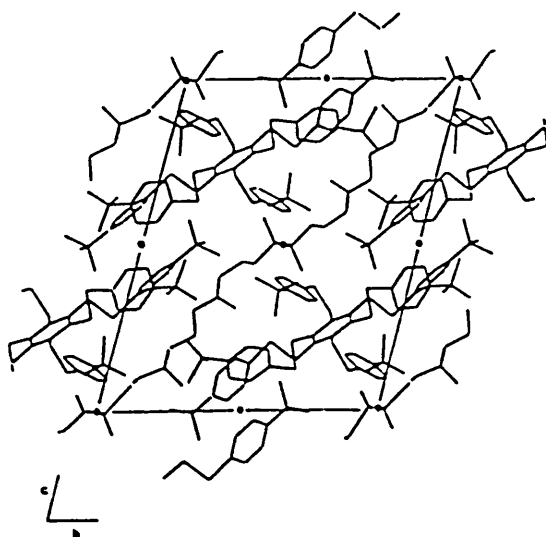
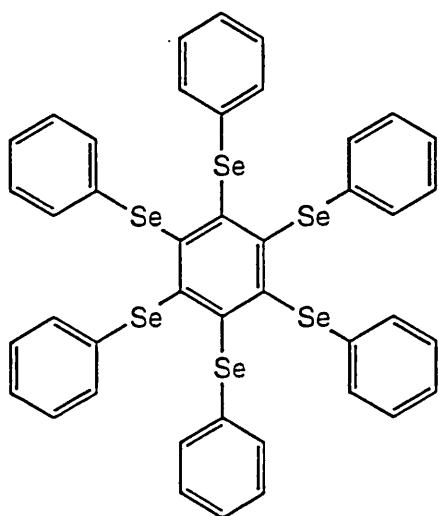


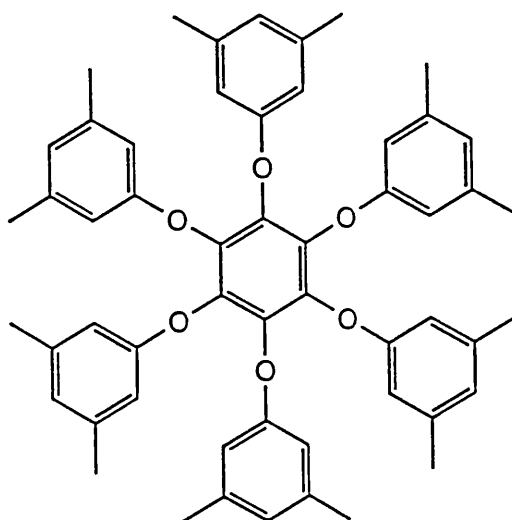
Fig. 40 A view looking onto the *bc* plane illustrating the host-to-guest packing in the adduct of (63) with squalene.

In all the hexa-hosts so far there has been a 3-fold symmetry with alternating up and down conformation round the central benzene ring (Fig. 40 (a)) (as the aromatic moieties do in the phenol hosts round the hydrogen

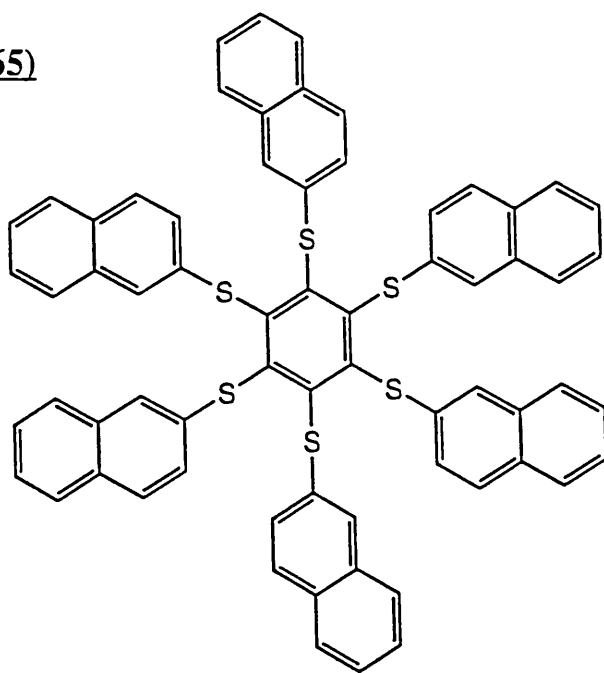
bonded hexamer). However, this altered when MacNicol used 1,3-dimethyl imidazolidin-2-one (DMEU)^{87,88} to overcome the synthetic problems of a one atom link. This resulted in a variety of one atom linked hexa-hosts, (65)–(67) are some of hosts obtained.



(65)



(66)



(67)

Although (65) and (66) adopt the normal 3-fold conformation (67) adopts a 2-fold conformation. The two different conformations are shown in Fig. 41.

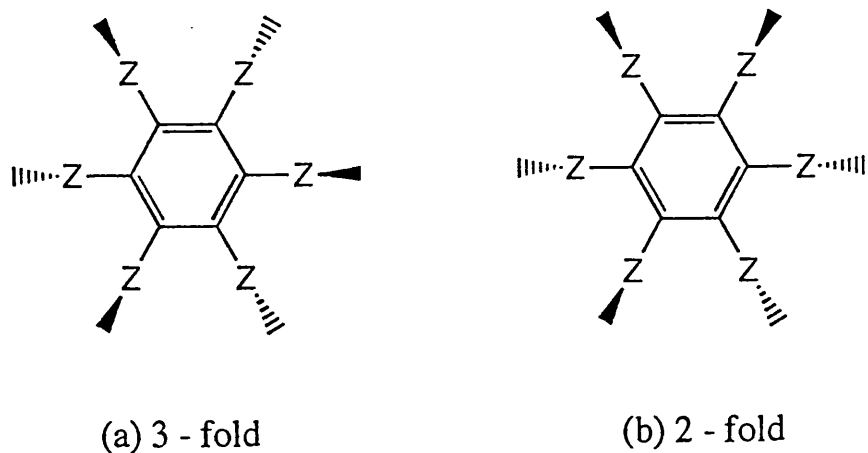


Fig. 41 The two conformations found in the hexa-hosts.

Even though (67) has changed its conformation away from the important 3-fold symmetry it does adopt a 2-fold symmetry which has also shown to be important in hosts, as detailed by Mak⁸⁹ (see also 3.4 - 3.5). Fig. 42 shows the packing of the adduct of (67) .1,4-dioxane⁹⁰.

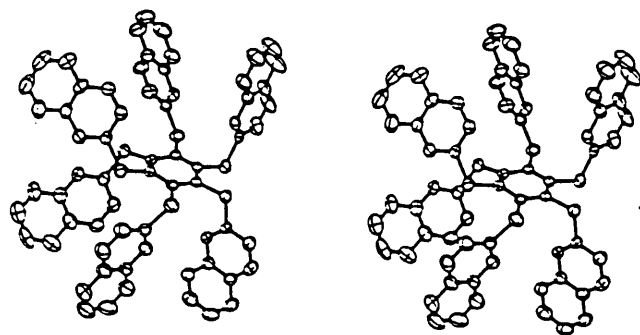
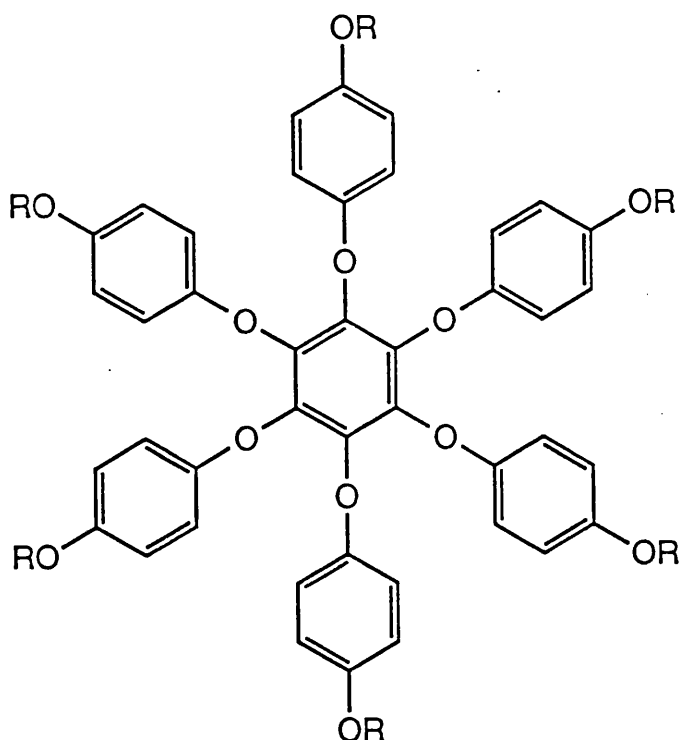


Fig. 42 A stereoview showing the host molecule of (67) in its 1,4-dioxane channel-type inclusion compound.

MacNicol then went on to introduce functionality into the host. All previous hosts have been of a Type I clathrate. He and co-workers synthesised the direct analogue to β -hydroquinone, hexakis(p-hydroxyphenoxy)benzene (69)⁹¹, prepared by reacting the methoxy ether (68) with boron tribromide.



(68) : R = Me

(69) : R = H

(69) forms two types of clathrate. The first includes six molecules of guest e.g. DMSO or pyridine and the second includes one molecule of a smaller guest e.g. H₂O or MeOH. The X-ray structure of the pyridine adduct is shown in Fig. 43 and shows that it corresponds to a Type III host. The MeOH adduct

corresponds to a Type II host (analogous to β -hydroquinone) (see results and discussion).

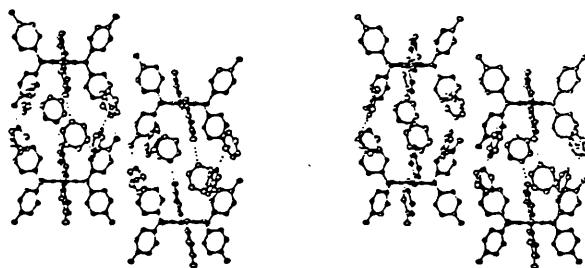
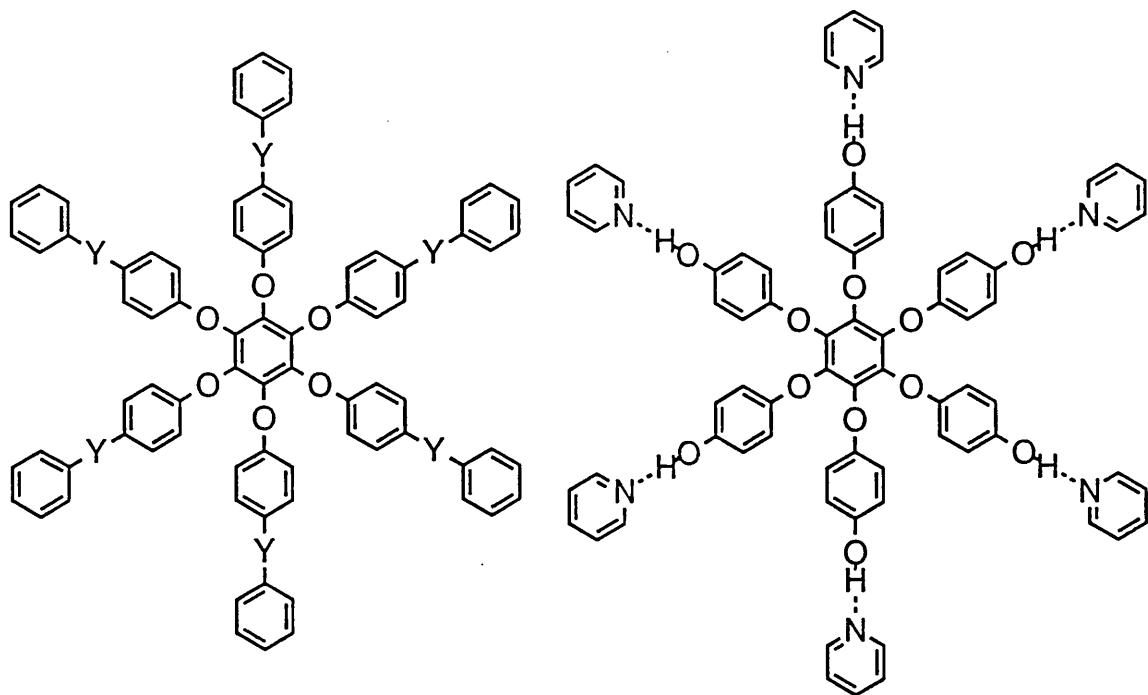


Fig. 43 A stereoview normal to the c -axis illustrating the intercolumn packing in the pyridine adduct of (69), H_2O molecules not shown.

The pyridine adduct also includes water, believed to be in the voids formed by the (69).pyridine complex. This led MacNicol to take the next step and replace these $\text{OH}\cdots\text{N}$ hydrogen bonds and produce new host compounds⁹².

Compounds (70)-(72) all include and Fig. 44 shows the similarity between (71). CH_3I clathrate and (69).pyridine clathrate. (70)-(72) are all examples of 3rd Generation hosts based on 3rd Generation hosts.



(70) : Y = O
 (71) : Y = CH₂
 (72) : Y = CMe₂

(69) . 6 pyridine

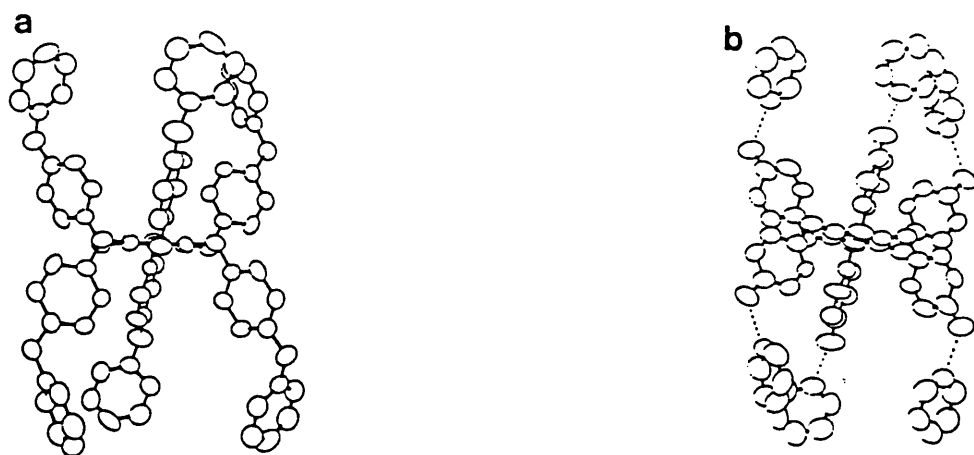
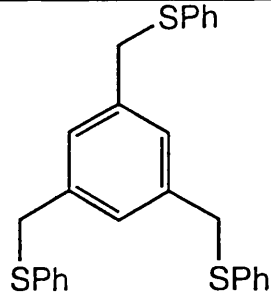
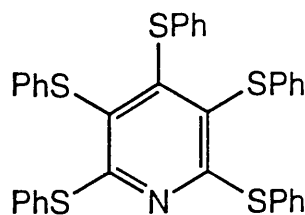


Fig. 44 A comparison of the molecular conformation of (71).CH₃I clathrate and (69).pyridine clathrate.

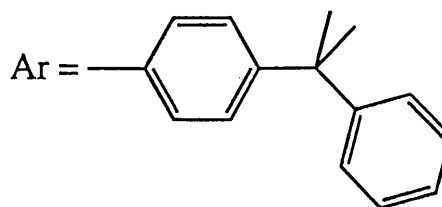
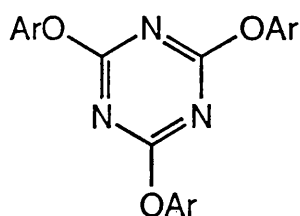
MacNicol also went on to consider the number of legs required for inclusion⁸⁴.



(73)



(74)



(75)

(73)⁸⁴, although trigonal, does not include, possibly due to the greater flexibility in the molecule. (74) does not include, possibly, due to lack of symmetry as well as rigidity. (75) on the other hand does show inclusion behaviour. (75) was chosen based on what is now called the 'Piedfort' concept⁹³. It was believed that it would double up and the dimer of the molecule would act as a hexa-host (Fig. 45).

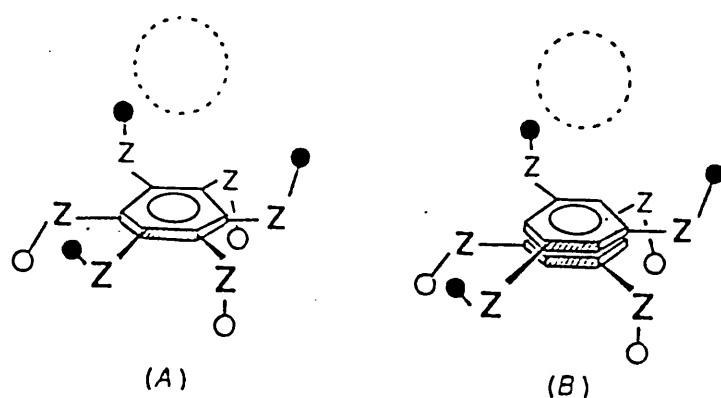


Fig. 45 A comparison of a typical hexa-host (A) with its 'Piedfort' analogue (B), composed of two trisubstituted (6π -electrons) aromatic rings juxtaposed. The light dotted circle is symbolic of the projected guest in each case.

(75) does indeed self-assemble into the dimer and Fig. 46 shows the packing of the clathrate with 1,4-dioxane and Fig. 47 shows the self-assembled dimer unit. The central 1,3,5-triazene rings are in van der Waals contact and correspond to the same staggered arrangement of nitrogen atoms found by calculation for the minimum energy of the dimer of 1,3,5-triazene itself⁹⁴. A possible reason why (73) does not form this dimer could be that the central ring is too electron rich, therefore, hindering π - π interactions¹³, whereas the triazene has its electrons more polarised on the nitrogens allowing stronger π - π interactions between molecules.

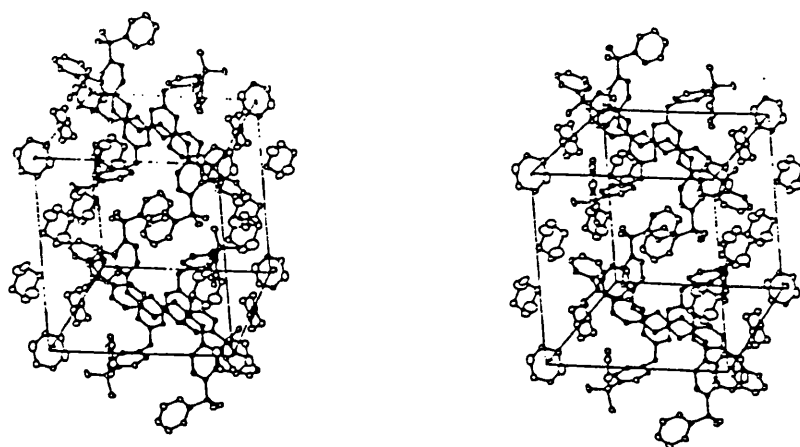


Fig. 46 Stereoview illustrating the host guest packing in the 1,4-dioxane compound of (75).

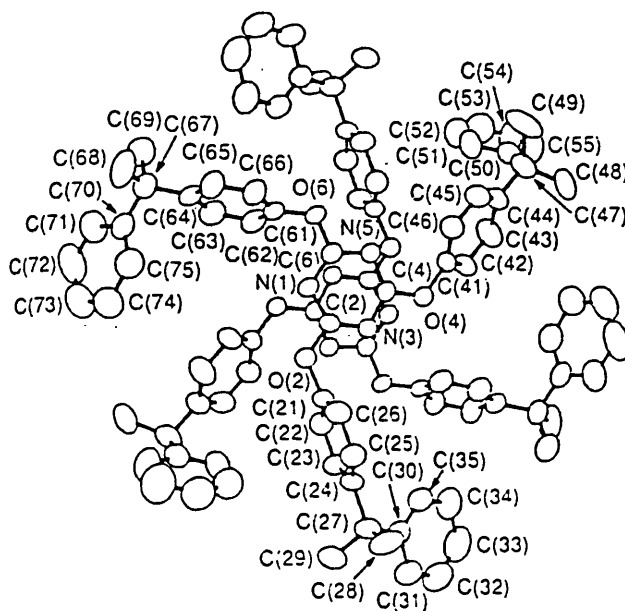


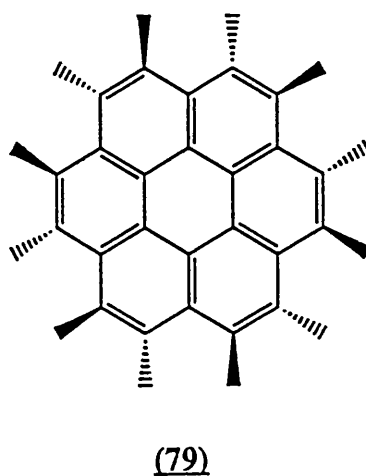
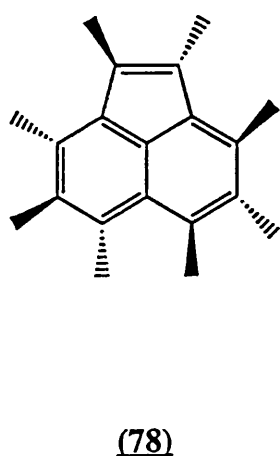
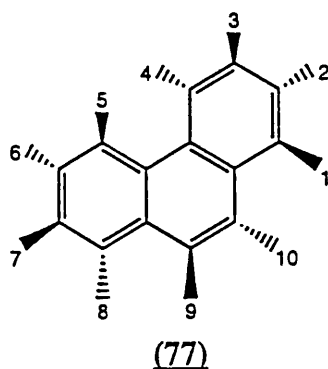
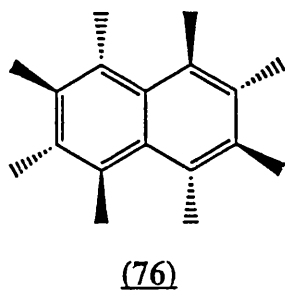
Fig. 47 A view of the Piedfort unit in the 1,4-dioxane clathrate of (75). The two central rings are accurately superimposed but for clarity the new direction is inclined to the normal of the central ring planes.

So although the hosts are not linked by hydrogen bonding, the fact they are linked by Π - Π interactions makes this a Type II clathrate.

3.6.2 Other Core Molecules

MacNicol and co-workers then went on to examine a series of cores other than benzene.

(76)-(78) were studied in order to try and take advantage of the C_2 symmetry they have (assuming alternate a,b legs). (76), the naphthalene core, produced a new series of clathrates called 'spider' hosts (80)-(83) are some of these inclusion compounds (80), the parent thio-leg, adopts a aabbaabb conformation (a-above core, b-below core) corresponding to an exact C_2 symmetry⁹⁵. (81) also adopts this conformation⁹⁶. Interestingly enough in this compound both unsolvated and solvated (81) adopt the same host packing. This means that even in the empty form there is a cavity (Fig. 48), which is completely symmetrical reflecting an efficient edge on packing of (81), (82) on the other hand adopts a different conformation abbabaab and so packs completely differently, however, (82) still includes although the cavity has lost all its symmetry (Fig. 49)⁹⁶.



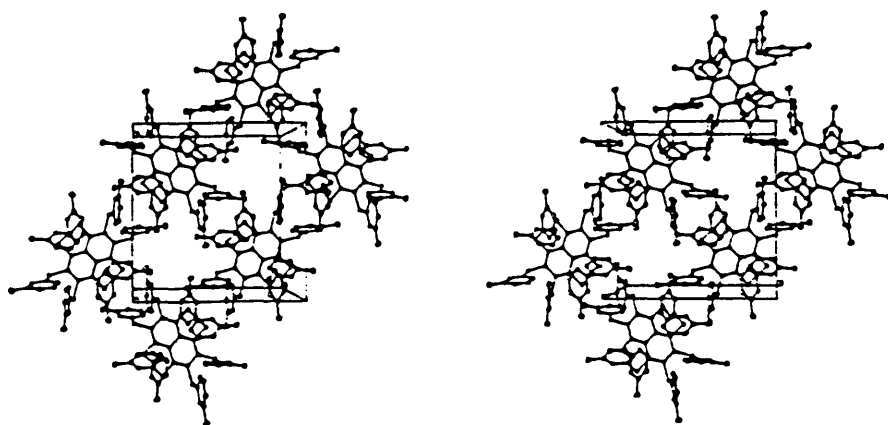
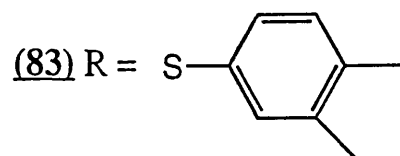
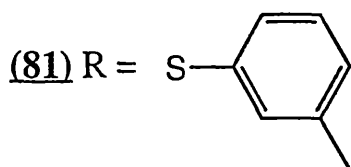
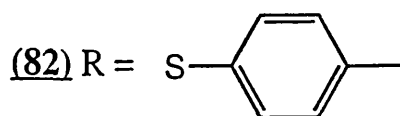
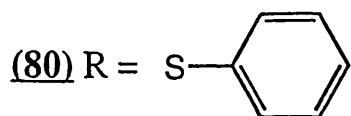
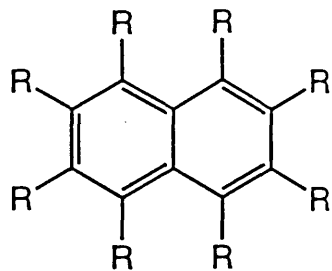


Fig. 48 A stereoview, looking down *c*, showing the molecular packing of (81) in its empty cage form.

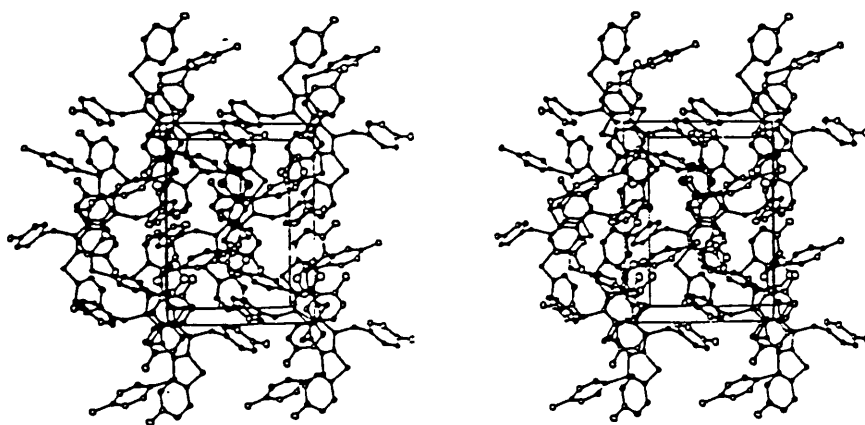


Fig. 49 A stereoview, looking down the *c*-axis of the host-guest packing in the 1,4-dioxane clathrate of (82). The atoms of the chair-shaped guest molecule closest to the viewer have been represented by filled circles for clarity.

Combination of the *m*-tolyl (81) and the *p*-tolyl (82) is the 3,4-dimethyl phenylthio counterpart derivative (83). It adopts a very similar conformational shape to (81) (Fig. 50), however, the extra *p*-methyl means the molecule packs in a different way as a clathrate. Fig. 51 shows the packing of (83).toluene adduct. (83) is the most versatile of all the spider hosts and includes a wide variety of different guests.

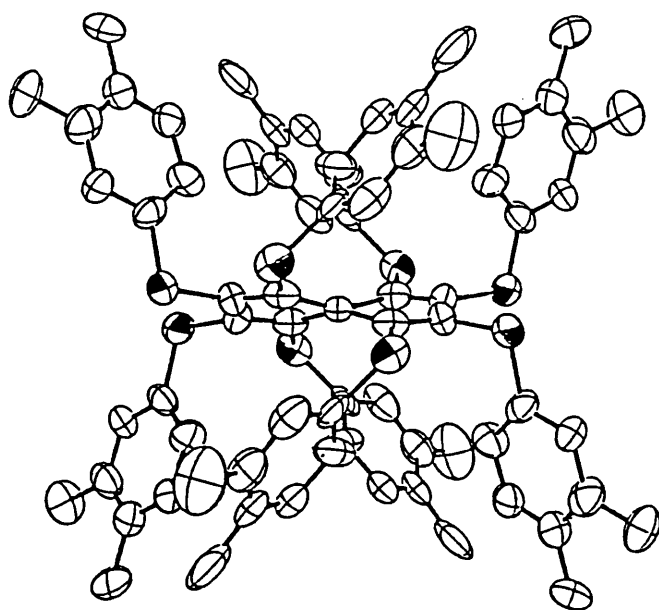
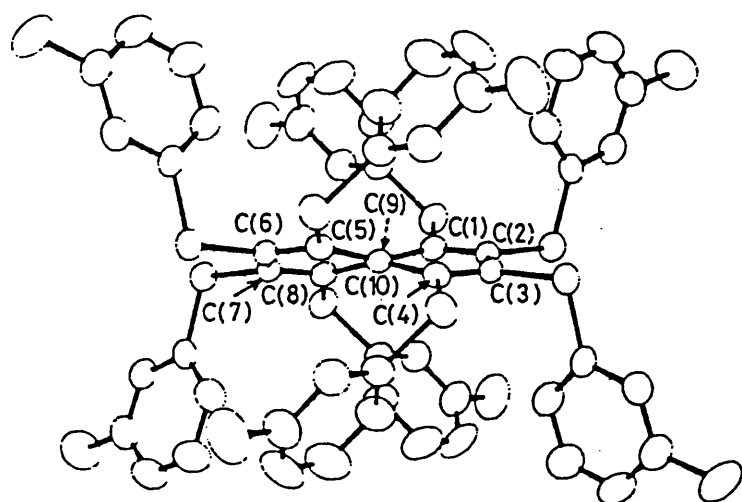


Fig. 50 Conformations of both (81) and (83).

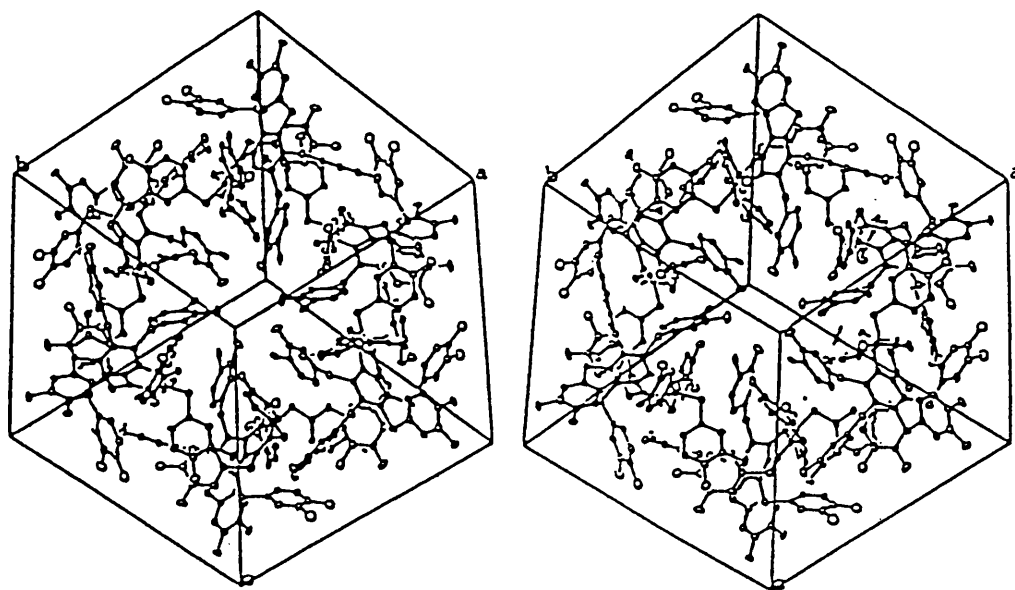
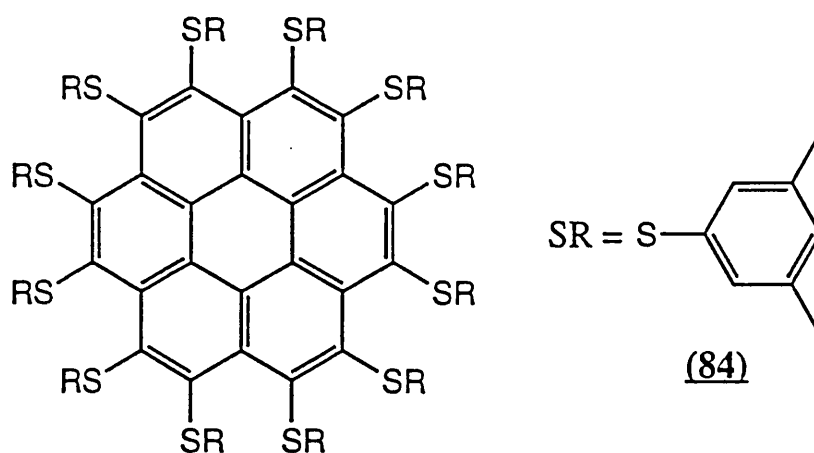


Fig. 51 A stereoview showing the molecular pack of (83).

Phenanthrene (77) and acenaphthalene (78) were examined but no inclusion behaviour was noted^{97,98}. A possible reason might be due to *peri* interactions between 5,4-substituted hetero atoms (in (77)) twisting the

aromatic core so much that any inclusion ability is destroyed and in (78) *peri* interactions between 2,3 and 1,8 are not enough to keep a rigid structure and, therefore, the greater flexibility of the 1,2,3 and 8 legs disrupt clathrate formation. It is also interesting to note that in (77) and (78) the axis of symmetry does not run perpendicular to the core as it does in benzene, triazene and naphthalene.

Coronene, (79) does form inclusion compounds and the packing of such clathrates can be seen from Fig. 52, which shows the clathrate of dodecakis-(3,5-dimethylphenylthio)coronene (84) and 1,4-dioxane⁹⁷.



(84) does adopt the (aabbbaabbbaabb) conformation required for general C_3 symmetry. There are two guest locations one being ordered the other disordered.

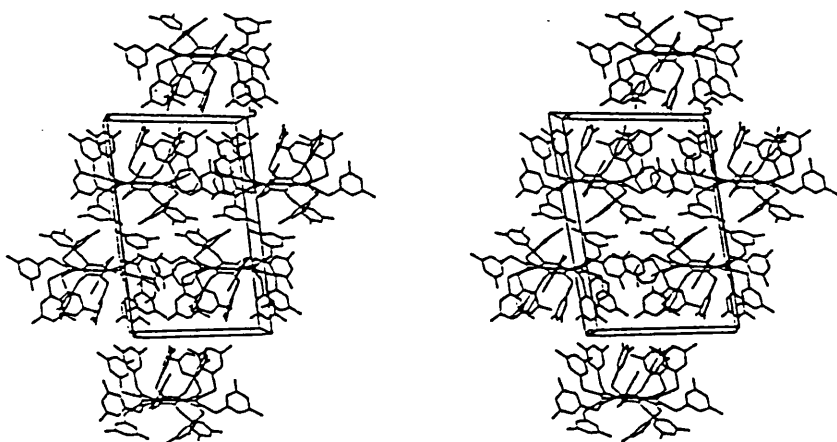
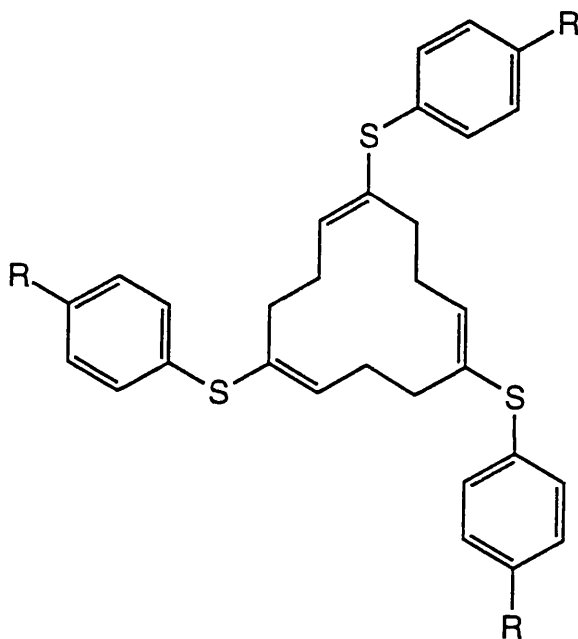


Fig. 52 A stereoview showing the host-guest packing in the 1,4-dioxane adduct of (84).

The fact that symmetry considerations, either C_3 or C_2 , went into designing the altered core hexa-hosts, means these are 4th Generation hosts. With this work MacNicol has demonstrated the importance of C_3 symmetry in the same way that Toda and Weber had done for C_2 symmetry.

3.6.3 Hosts Designed by Pure Symmetry Considerations

MacNicol had now shown the importance of C_3 symmetry so he went on to design molecules with 3-fold symmetry in order to come up with a new series of 4th Generation hosts. This he duly did with the cyclododecatriene based hosts (85) and (86)⁹⁹.



(85) : R = H

(86) : R = Me

Both hosts included numerous different guest molecules, however, no X-ray study of any adduct has yet been reported.

3.7 Buckminster Fullerene (C₆₀) and Derivatives

The recently topical C₆₀ molecule was first used in an inclusion compound as a proposed guest for hydroquinone by Ermer³⁷ (see Section 3.3.1)

in 1991, but it was not until 1992 when Kroto¹⁰⁷, looking for a way to stop the spherical C_{60} rotating in the crystal lattice so bond lengths could be determined, was C_{60} actually used as a host, with benzene as a guest. Further studies were carried out and other guests such as ferrocene¹⁰², iodine¹⁰³ and diiodomethane¹⁰⁴ were discovered.

Two distinct types of clathrates are formed. The first is seen in the benzene clathrate¹⁰⁵ where the benzene molecules lie in large channels between columns of C_{60} molecules (Fig. 53).

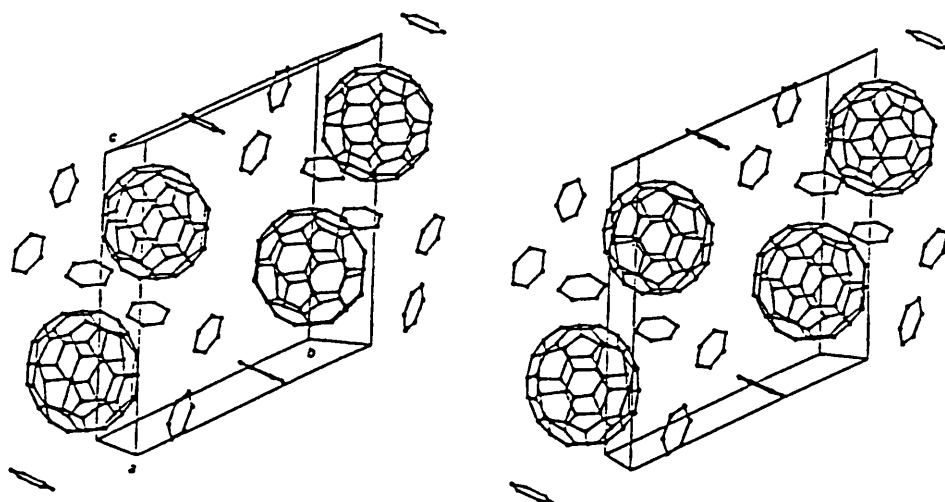


Fig. 53 A view of $C_{60} \cdot 4C_6H_6$ down the crystallographic a axis.

The other type is more common and is a layered structure. This is seen in the adducts of iodine, ferrocene, diiodomethane. Fig. 54 shows the ferrocene clathrate. It is interesting to note that there are believed to be interactions between ferrocene and C_{60} and CH_2I_2 and C_{60} suggesting that these might be Type III clathrates.

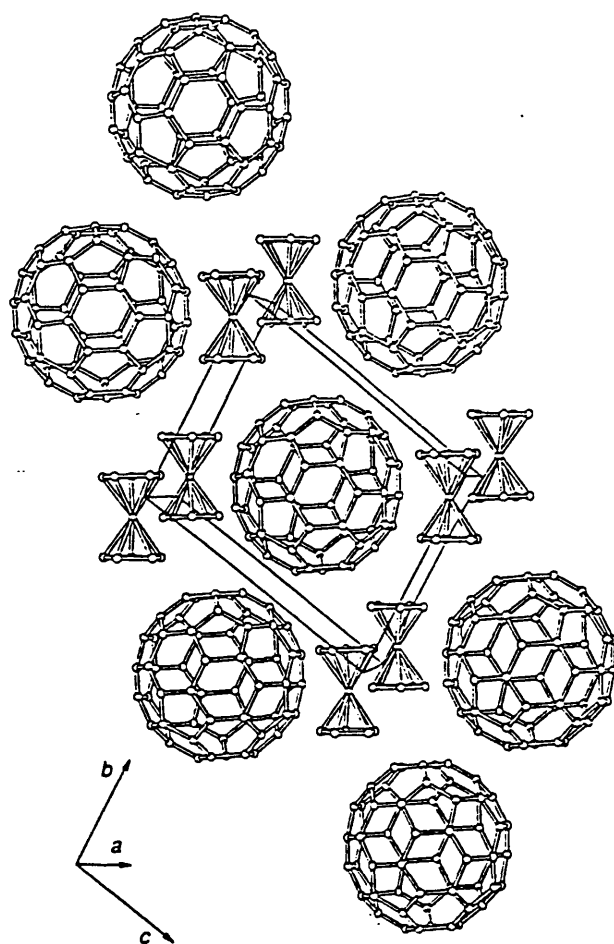
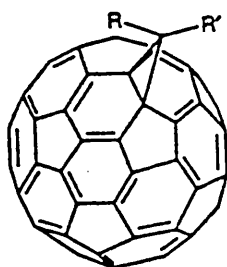


Fig. 54 Packing arrangement for $C_{60}(\text{ferrocene})_2$ in the bc plane.

In view of this it could be suggested that in $C_{60}(\text{hydroquinone})_3$, because the C_{60} has an equal volume and greater mass than the hydroquinone, that it is the host and the hydroquinone is the guest.

An interesting appendage to this section on C_{60} hosts is the recent discovery that the methano-fullerene (87), by Vögtle¹⁰⁶, includes chloroform.



(87) $R = \text{Ph}$, $R' = 3,4\text{-(MeO)}_2\text{Ph}$

Fig. 55 indicates host-host interactions and host-guest interactions (but only to 1 of the chloroforms) and Fig. 56 shows the zig-zag chain of molecules in the clathrate.

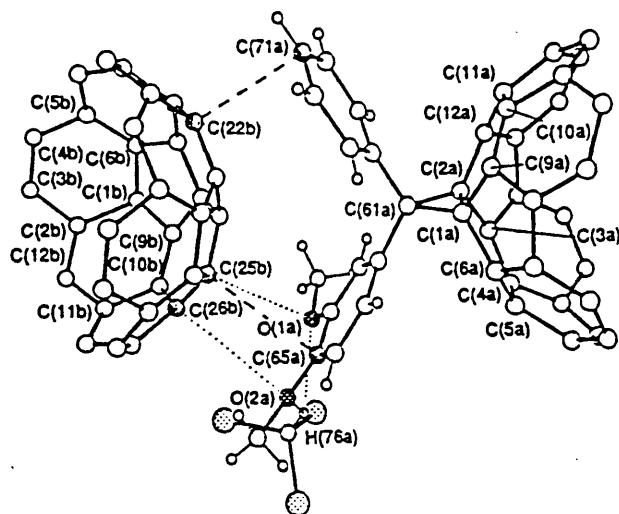


Fig. 55 Section of the crystal packing of (87).2CHCl₃ indicating intermolecular contacts between two phenyl groups and the nearest neighbouring fullerene.

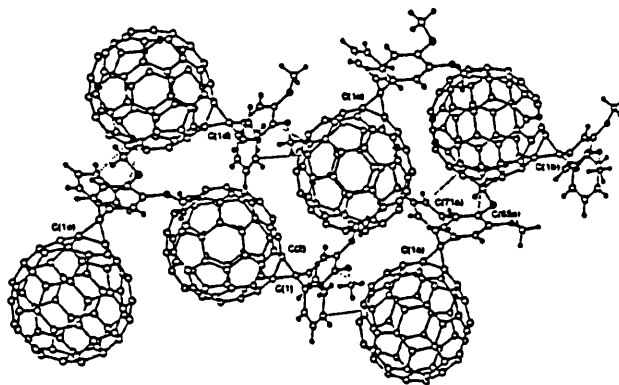


Fig. 56 Zig-zag chains in the crystal packing of (87) (CHCl₃ omitted).

This could be considered as an extension of Webers theory on design of coordinato-clathrates (see Section 3.5) with the bulky skeleton being the C₆₀ moiety. This makes fullerene a potential source for many interesting novel clathrates.

4. USE OF CLATHRATES

As design and structural elucidation of clathrates continues to advance, investigation into the uses of such compounds is becoming more and more important. The uses of clathrates can be categorised into three main sections

- (1) Separation and Isolation
- (2) Storage and Stabilisation of Reagents
- (3) Photoreactions

The purpose of this chapter is to illustrate these properties and applications.

4.1 Separation

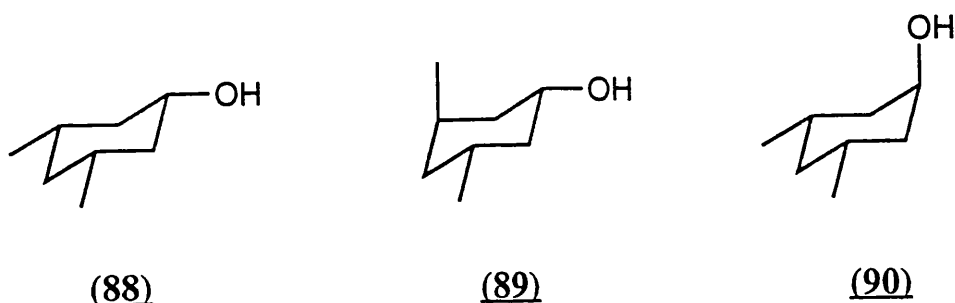
Host-guest complexation is a very effective method for the separation of isomers, especially those isomers which have boiling points too close to separate by distillation.

4.1.1 Separation of Isomers

Separation of *o*, *p* and *m*-isomers of disubstituted benzenes have been investigated by a number of groups and enclathration proved to be a successful way of separating these isomers, for example 1,1,6,6-tetraphenylhexa-2,4-diyne-1,4-diol (22) can be used to separate *o*- and *p*-isomers^{54,107,108}. It forms

inclusion complexes with the *p*-isomer only and so upon heating of the crystals, in vacuo, 100% pure *p*-isomer is recovered. From the filtrate left, 95% pure *o*-isomer can be obtained by distillation in vacuo, in 90% yield.

(22) has also been used to separate aliphatic compounds. (88) can be isolated from a mixture of (88), (89) and (90). (88) possesses only equatorial substituents and so forms more stable complexes with (22)^{108,109}.

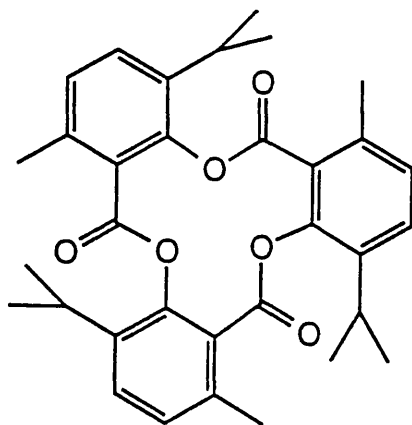


4.1.2 Separation of Enantiomers

The separation of enantiomers is based on the formation of diastereomeric inclusion compounds, e.g. (*R*)-host.(*S*)-guest and (*R*)-host.(*R*)-guest, conferring on the enantiomeric guests different physical properties and allowing them to be separated by crystallisation.

There are two main ways that can be used in order to obtain a chiral cavity, which is required for chiral resolution. The first is the use of a chiral host and the other is the formation of chiral channels using an achiral host. An example of the latter type of chiral cavity formation is urea which forms chiral helix channels¹¹⁰.

Inclusion compounds with cages tend, in general, to be more effective, than those with channel cavities, for optical resolution. This can be seen in tri-o-thymotide (91) which forms cages with small guests, 2-chlorobutane (e.e. 32%-(*S*)) and channels with larger guests, 2-chlorooctane (e.e. 4%-(*S*))¹¹¹.

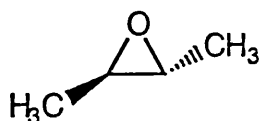


(91)

Some of the other main things that can effect enantiomeric selectivity are :

(a) Rigidity of cavity. This can be of crucial importance in avoiding either enantiomer of the guest adjusting the chiral cavity and hence allowing both of them to be included.

(b) Cavity symmetry and guest symmetry. If the guest and cavity have the same symmetry then a higher e.e. is obtained. For example, the guest trans-2,3-dimethyl-oxirane (92) has a 2-fold molecular symmetry which is also the symmetry of the cavity in (91), where the guest is located in the crystal¹¹², this guest exhibit higher selectivity (e.e. 47%-*S,S*) than those without symmetry¹¹¹.



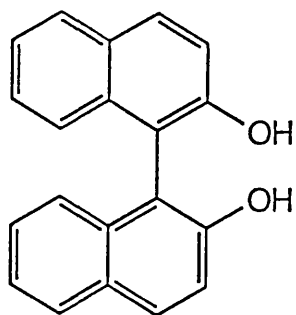
(92)

(c) Guest size - the fit of the guest must be tight, if too small either enantiomer can be incorporated into the cage and if too large the guest can disrupt the shape, and hence chirality of the cage.

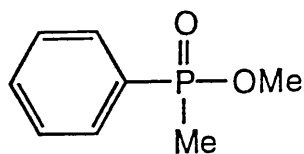
(d) Temperature - if the cavity is not rigid enough, then at higher temperatures racemisation can occur. This is shown in the racemisation of $\text{CH}_3\text{S}(\text{O})\text{OCH}_3$ in (91)¹¹³ when heated at 125°C for 12 hrs. It was shown, by powder photography that, before and after the heating, the cage clathrate structure was not destroyed suggesting that racemisation takes place within the cavity of (91).

(e) Finally, an important consideration is the interactions between host and guest. These types of inclusion complexes exhibit the best ability to resolve guests. 2,2'-Dihydroxy-1,1'-binaphthyl (93) has been used to resolve a wide variety of sulfoxides, sulfoximines, selenoxides, phosphine oxides and

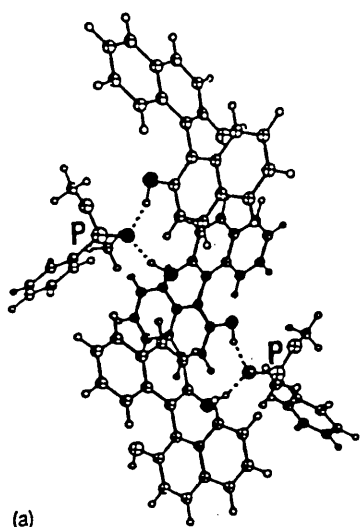
phosphinates⁵ all in approx. 100% e.e. Figures 57 and 58 show the bonding between (+)-(94) and (+)-(93) or (-)-(93) respectively.



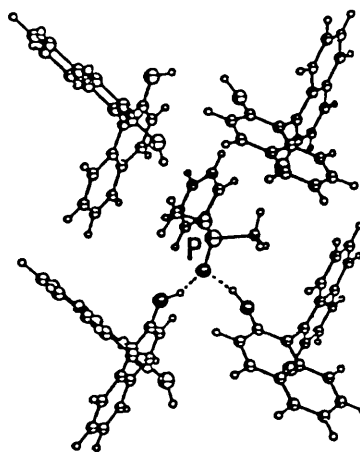
(93)



(94)



(a)



(b)

Fig. 57 Crystal structure of the (*R*)-(+)-(93).(+)-(94) inclusion compounds; packing illustrations: (a) view of the H-bonding interactions between host and guest, (b) view of the crystalline host environment around the guest molecule. O atoms are represented by large spheres.

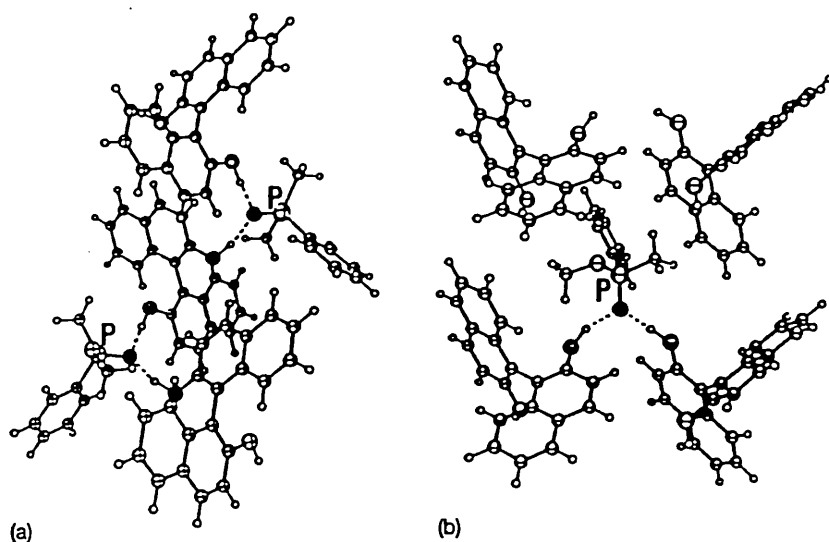


Fig. 58 Crystal structure of the (S) -(-)-(93).(+)-(94) inclusion compound: (a) and (b) as for Fig. 57.

The crystal structures⁶⁸ of these two compounds are characterised by some similar features. They both consist of continuous chains of hydrogen bonded species. In these chains, the polar $P=O$ group acts as a proton acceptor from two different host molecules, however, it is the methoxy and methyl substituents on the phosphorous that cause the difference in topological complementarity between host and guest molecules. In (S) -(-)-(93) with (+)-(94) the methoxy group is turned inward (with respect to the hydrogen bonding site), however in the (R) -(+)-(93) clathrate the methoxy group is turned outward, thus keeping the chains at a distance so making this lattice less densely packed than the (S) -(-)-(93) lattice with (+)-(94) ($D_c = 1.282$ vs. 1.300

gcm^{-3}), and so less stable which is in agreement with the observed enantioselectivity, which is (+) prefers (-).

The only disadvantage with this type of resolution is that the guest requires an appropriate bonding site in order to complex the host.

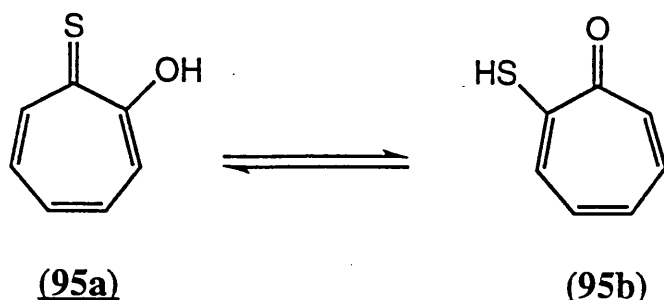
4.1.3 Isolation of Natural Products

Toda has used his versatile diol host **(22)** to isolate natural products from their raw starting materials¹¹⁴. For example, caffeine, nicotine and cholesterol can be isolated from tea leaves, tobacco leaves and gall stones, respectively.

This was easily achieved by refluxing the raw material in an organic solvent and then adding the host and recrystallising to obtain the natural product adduct. In this way up to 82% of the natural product could be obtained and provides a quick and easy method of isolating natural products.

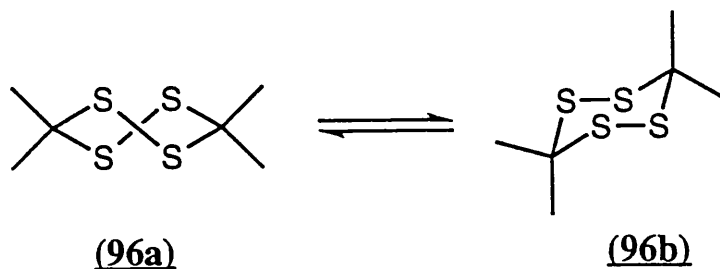
4.1.4 Separation of Equilibrium Mixtures

(22) has also been used to separate out tautomers. 2-Mercapto substituted tropone **(95)** exists mainly in the 2-hydroxytropothione **(95a)** rather than the 2-mercaptotropone **(95b)** both in solution and solid state, however, **(95b)** can be isolated in the form of an inclusion complex with **(22)**¹¹⁵.



The isolation of the less abundant tautomer is due to hydrogen bonding between (22) and the carbonyl oxygen of (95b).

The hexa-hosts have been used to isolate out conformational isomers. The twist-boat form (96a) of 3,3,6,6-tetramethyl-s-tetrathiane is substantially favoured over the less stable chair conformer (96b). In order to try to isolate (96b) in the solid state MacNicol and Murphy believed that because of the symmetry distinction between the centrosymmetric chair form (96b) and the chiral twist-boat form (96a), it might be possible to isolate (96b) within a cavity of an inclusion compound. This was done utilising hexakis(*p*-*t*-butylphenylthiomethyl)benzene (63), as the host, to yield (96b), at -90°C , in solution with a purity of $>95\%$ ¹¹⁶.



MacNicol suggested that trapping of guests in such novel conformations offers the possibility of specific guest reactions.

4.2 Storage and Stabilisation of Reagents

Molecular packaging, the storage and stabilisation of guest molecules within crystalline host lattices, has been known for some time¹¹⁷ examples being the protection of unsaturated fatty acids in urea^{118,119} and ascaridole or vitamin D₃ in β -cyclodextrin¹²⁰. Only recently, however, has attention been directed towards the lattice storage of chemical reagents, especially those which, for example, are pyrophoric, hydrolytically unstable, volatile or toxic in the free state. The aim of the present chapter, representing a review of the subject at an early stage of development, is to illustrate how suitable crystalline supramolecular assemblies can be employed for effective reagent containment. It should be appreciated that potential uses as well as established applications are highlighted.

Important criteria that an effective host lattice must meet are :

- (a) tight retention of desired guest, until its release is required;
- (b) effective protection of guest from external agents such as air, moisture, CO₂ or light, etc;
- (c) facile and quantitative release of intact guest when required;
- (d) the compound comprising the host lattice (if present during reaction) should be inert and capable of being recycled, if appropriate.

In the following sections, describing organic and inorganic host lattices, two types of behaviour are found on guest reagent release: in the first case the free guest is liberated and normal reagent activity is expected; in the second case, owing to the presence of the host component, the reagent gives different products or product distribution from that normally encountered.

4.2.1 Use of Organic Host Lattices for Reagent Containment

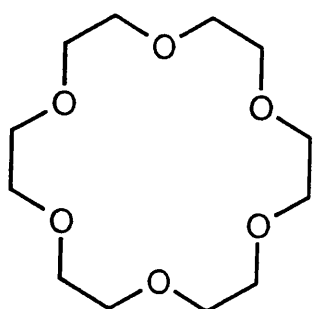
4.2.1.1. Crown-complexed Reagents

Crown compounds, versatile complexing agents, are potentially useful as hosts for storage of many different types of reagents and unstable species.

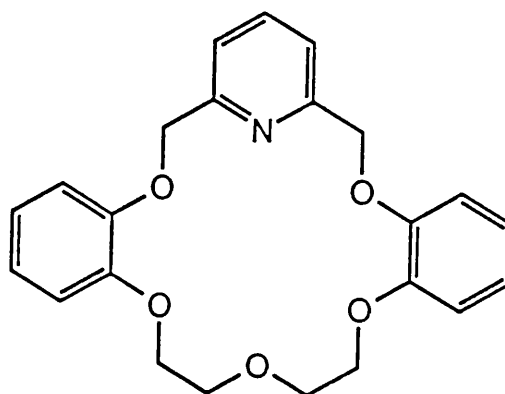
Vögtle and Müller¹²¹, recognising the significance of intermolecular

C-H...O host-guest interactions¹²², have prepared a number of crystalline crown complexes containing volatile and highly toxic reagents possessing weakly acidic methyl or methylene groups. Examples are containment of dimethylsulphate and methanesulphonyl chloride by 18-crown-6, (97) and *N,N*-dimethylnitrosamine by dibenzopyridino[18]crown-6, (98). The complex of (97) with CH₃SO₂Cl, host-guest ratio 1:2, readily converts cholesterol into its *O*-mesylate; host (97) remains intact and can be recovered. The vapour

pressure of the complexed reagents is low and no smell of guest is noticeable. Chloroacetonitrile also forms a crystalline complex with (97) and this adduct, also consolidated by C-H...O interactions, has been studied by X-ray diffraction and ^{13}C CPMAS NMR methods¹²³.



(97)



(98)

Crown complexation has been used to stabilise reactive Lewis acids by direct coordination¹²⁴⁻¹²⁸, as for TiCl_4 , AlMe_3 , AlEt_3 and GaMe_3 . Second sphere coordination¹²⁹, involving OH...O hydrogen bonding, has been found¹³⁰ to stabilise the rather unstable hydrate, $[\text{H}_2\text{O}\cdot\text{BF}_3]$ as the 1:1:1 complex with crown (97); and the dihydrate of silicon tetrafluoride (*trans*- $\text{SiF}_4\cdot 2\text{H}_2\text{O}$) has been structurally elucidated in a related complex with the same host¹³¹.

Atwood and co-workers¹³² have described the novel stabilisation of the highly reactive $[\text{AlMe}_2]^+$ cation, of interest with respect to Ziegler/Natta catalysis with donor systems, within the voids of crown (97) and 15-crown-5.

In the larger crown the cation is angular, Me-Al-Me angle $140.6(3)^\circ$, in the smaller crown the guest cation is effectively linear, Me-Al-Me angle $178(1)^\circ$.

Calixarenes^{133,134} have also been used to stabilise Lewis acids in a similar way to crown hosts. However, the calixarene complexes appear to be, in general, less reactive.

A useful method for stabilising metal ozonides as complexes which are soluble in a wide range of solvents has been described by Korber and Jansen¹³⁵. The crystal structure of a representative complex, (97), i.e. $(\text{Rb})\text{O}_3\cdot\text{NH}_3$, is shown in Fig. 59. The crown has effective D_{3d} symmetry with the Rb^+ ion, too large for the cavity, displaced by *ca.* 1 Å from the mean plane of the ligand.

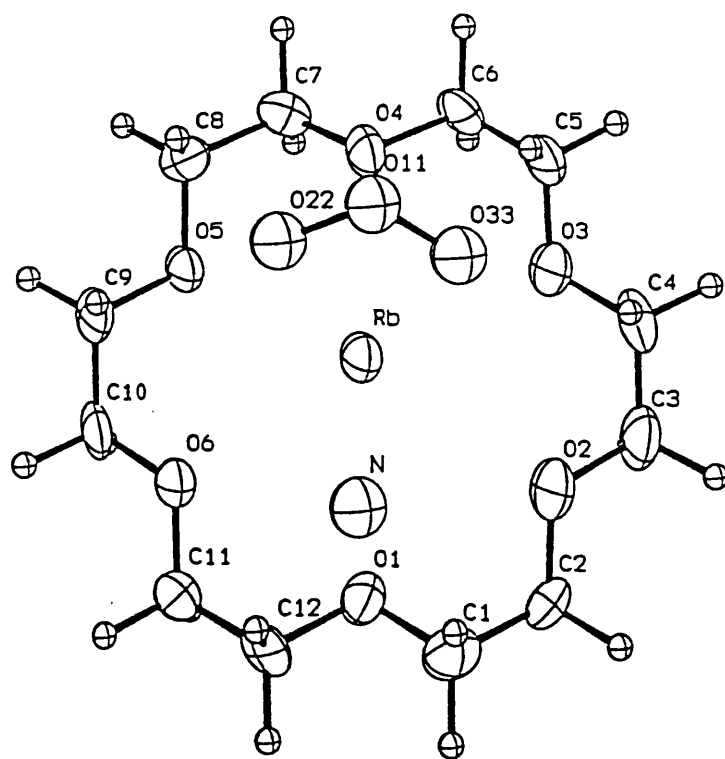
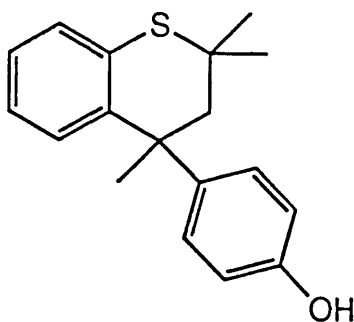


Fig. 59 An ORTEP-plot of $([\text{18-crown-6}]\text{Rb})\text{O}_3\cdot\text{NH}_3$ viewed normal to the mean plane of the crown (Ref. 135).

4.2.1.2 Storage of Reagents in Clathrates

The design and synthesis of new hosts capable of forming crystalline inclusion compounds extends the range of guest molecules which can be included and stored. Thus the host 4-*p*-hydroxyphenyl-2,2,4-trimethylthiachroman (7), more soluble than its parent Dianin's compound, 4-*p*-hydroxyphenyl-2,2,4-trimethylchroman, on recrystallisation from neat liquid dimethylmercury¹³⁶, forms a beautifully crystalline air-stable adduct with host-guest ratio of 6:1. The closed nature of the clathrate cage⁴³, which contains one Me₂Hg molecule, prevents guest loss.



(7)

The development of the hexa-host series¹³⁷ is also important with respect to guest storage. The hexa-host molecule hexakis(*p*-phenoxyphenoxy)benzene (70), a covalently linked and less reactive analogue of the host-guest unit found in the pyridine adduct of hexakis(*p*-hydroxyphenoxy)benzene⁹¹, has been

prepared with the specific purpose of containment of small reactive guest species¹³⁷. The host packing, which mimics closely the host-guest arrangement in the hydrogen-bonded pyridine progenitor, is illustrated for the 1:1 COCl_2 clathrate of (70) in Figure 60. The IR spectrum shows the $\nu(\text{C}=\text{O})$ band of phosgene in the clathrate at 1803 cm^{-1} , and release of the guest into a vapour phase IR cell gives a spectrum in agreement with a reference vapour spectrum. Host (70) has also been used to store¹³⁷ thiophosgene, thionyl chloride, and methyl iodide. The hexa-hosts hexakis(phenylthio)benzene¹³⁸ $\text{C}_6(\text{SPh})_6$ and hexakis(phenylseleno)benzene¹³⁹ $\text{C}_6(\text{SePh})_6$ have been shown to form clathrates with the synthetically useful materials CCl_3SCl and CBr_4 respectively.

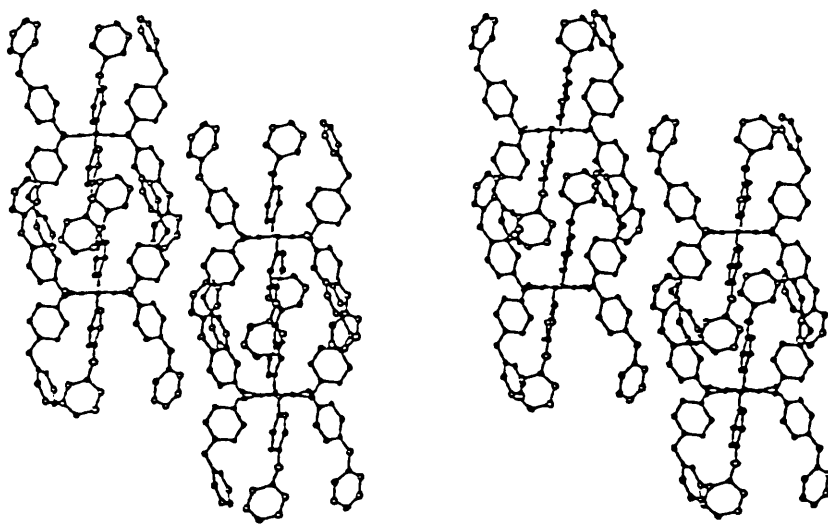


Fig. 60 A stereoview illustrating the efficient packing of adjacent columns which extend infinitely along c in the 1:1 COCl_2 clathrate of (70). The disordered phosgene molecule has been omitted for clarity (Ref. 137).

In contrast to the fairly labile 1:6 (host-to-guest) adducts of hexakis(*p*-hydroxyphenoxy)benzene (69) with pyridine or DMSO⁹¹, extremely stable adducts are formed with small guest molecules. X-ray crystallographic studies of the MeOH clathrate¹⁴⁰ have established that the host lattice has a double interlocking network structure analogous to that of β -hydroquinone¹². The very tight retention⁹¹ of MeOH by this form of the hexa-host, along with its relative oxidative stability and water insolubility, offer advantages over hydroquinone with respect to storage of volatile guests. Preliminary experiments¹⁴⁰ to include H₂ in this host have indicated that hydrogen is incorporated, analysis by mass spectrometry, but that this very small guest is lost over a period of several months. Hydroquinone itself has been studied as a method of storage of ⁸⁵Kr from nuclear power plant off-gases¹⁴¹: this suggests the possible use of hexakis(*p*-hydroxyphenoxy)benzene for longer-term storage of this radioactive guest.

Other representative phenolic hosts capable of retaining volatile guests (illustrative examples of guests shown in parenthesis) are phenol (100) (H₂S, HCl, HBr, CH₂=CHF), *p*-fluorophenol (101) (H₂S, CH₃Br), and Dianin's compound (6) (I₂, SF₆); these hosts have been reviewed elsewhere¹². The (CF₃SO₂)₂CH₂ clathrate of Dianin's compound has been used as a latent curing catalyst in cationic polymerisation¹⁴².

Bishop and co-workers have investigated the potential of the versatile host 2,7-dimethyltricyclo[4.3.1.1^{3,8}]undecane-*syn*-2,*syn*-7-diol (102) as a

chemical storage system¹⁴³. This host forms two types of lattice inclusion compound dependent on the size and shape of the guest, a helical tubular structure with CBr_2F_2 , of lower stability, and an ellipsoidal clathrate with the smaller guest CS_2 , which is considerably more stable. Fig. 61 shows the CS_2 guest sandwiched between two quartets of diol molecules in the ellipsoidal clathrate, and illustrated the potential to store small, volatile guest molecules.

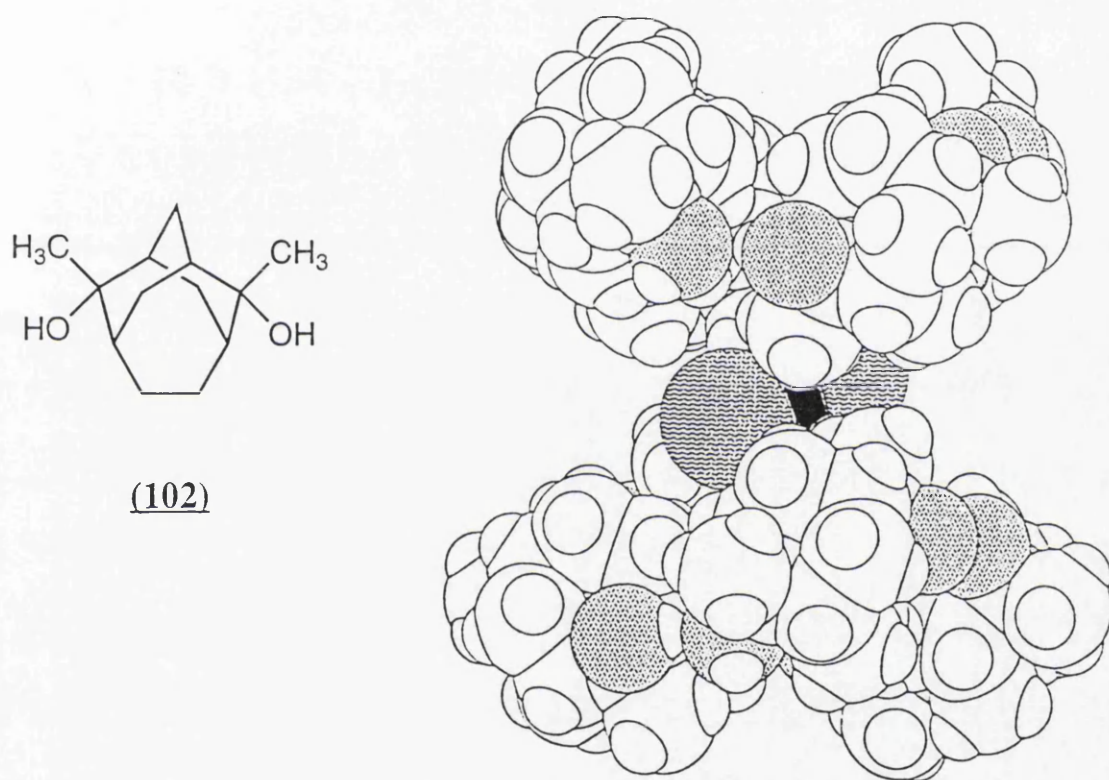


Fig. 61 Arrangement of the major orientation of the CS_2 guest in structure $(102)_4 \cdot (\text{CS}_2)$ viewed along b . The guest occupies an ellipsoidal cavity between cyclic quartets of the diol host. In this view, with the c -axis vertical, the top quarter of diols is from one sub-lattice and the bottom quartet from the other. Thus the guest is wedged between the two interpenetrating sub-lattices (Ref. 143).

Following earlier reports that the fullerene C_{60} forms inclusion compounds with molecules as diverse as benzene^{101,105}, iodine¹⁰³ and ferrocene¹⁰², Green and co-workers have very recently reported¹⁴⁴ the synthesis and characterisation of the inclusion complex $\{(P_4)_2C_{60}\}$. The structure of the black-blue solid is illustrated in Fig. 62, the tetrahedral P_4 molecules being located between layers of the C_{60} host. In contrast to the highly pyrophoric nature of free white phosphorus, the complex of P_4 with C_{60} is quite stable to air¹⁴⁴. Another fullerene complex, also corresponding to a mixture of allotropes of different elements $C_{76}(S_8)_6$, has been structurally characterised¹⁴⁵.

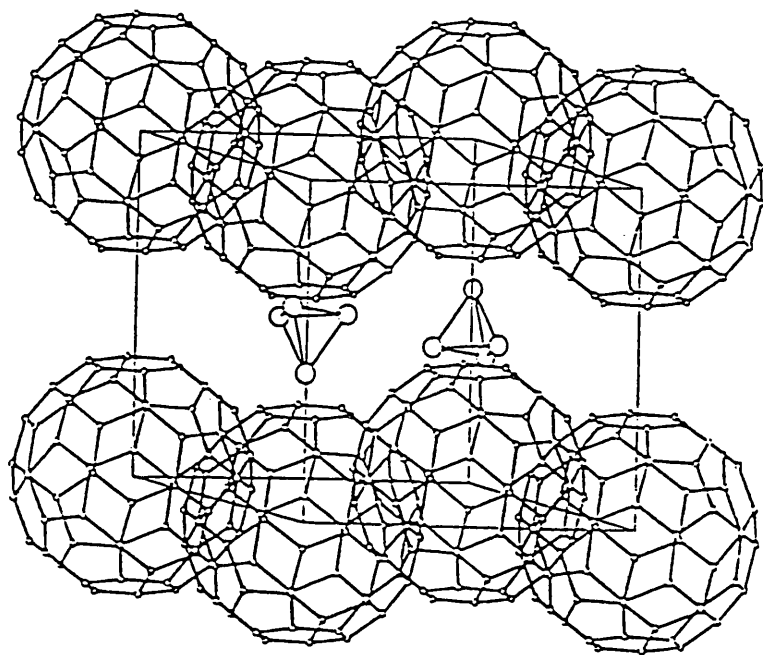


Fig. 62 Structure of $\{(P_4)_2C_{60}\}$. Only one orientation of the P_4 tetrahedron at each trigonal prismatic site is shown, corresponding to the space group $P3$ (Ref. 144).

4.2.1.3 Storage of Reagents in Other Organic Hosts

Hydrogen-bonded complexes of 2,2-di(*p*-hydroxyphenyl)propane (103) are formed with ammonia, amines and hydrazines from aqueous solutions and provide an anhydrous form of these guest species, which can be released upon heating¹⁴⁶. In the case of methylhydrazine, for example, a cyclic centrosymmetric hydrogen-bonded host-guest assembly is found, Fig. 63.

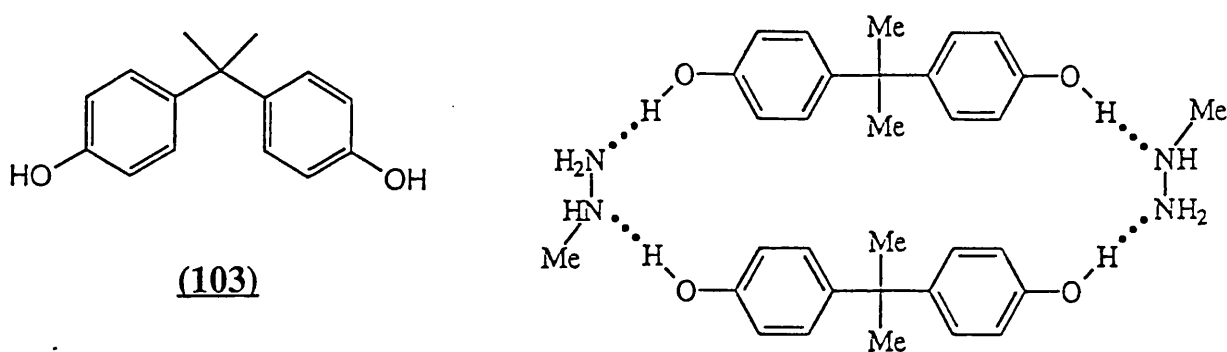
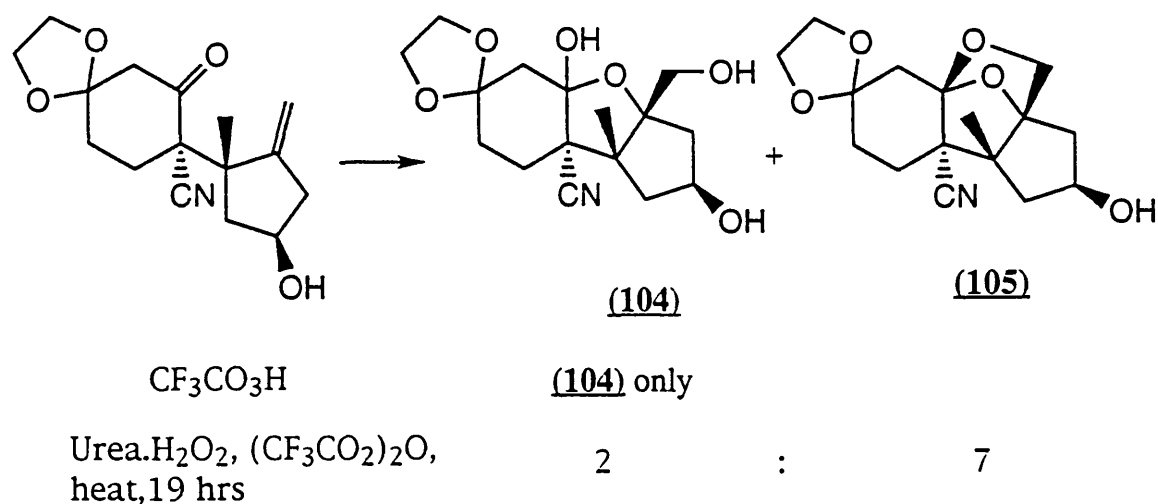


Fig. 63 Schematic representation of the host-guest unit in the 1:1 complex of (103) with methylhydrazine (Ref. 146).

Crystalline inclusion compounds of 2,2'-dihydroxy-1,1'-binaphthyl (40) with ammonia, and alkali metal hydroxides have also been described⁶⁴.

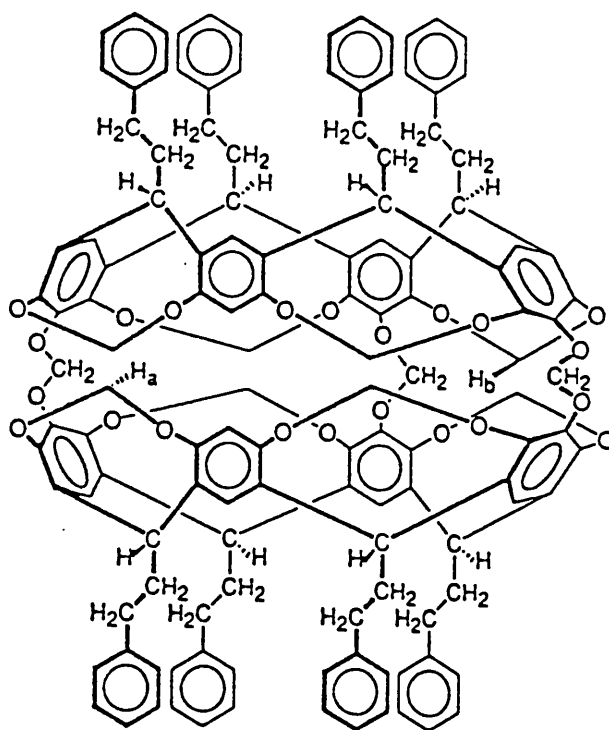
Studies into the storage of hydrogen peroxide as crystalline complexes with urea (2), 1,4-diaza[2.2.2]bicyclooctane (DABCO) and triphenylphosphine oxide have attracted recent attention¹⁴⁷. The urea adduct, apparently stabilised

by N-H...O hydrogen bonding between urea and hydrogen peroxide¹⁴⁸, is a quite crystalline solid providing a synthetically useful source of H₂O₂. Although this complex can often be used in place of conventional peroxides, a few interesting cases are known where different products are obtained, for example, Ziegler and co-workers¹⁴⁹ attempting to synthesise spiroacetal **(105)**, by epoxidation and subsequent cyclisation with CF₃CO₃H obtained only the hemi-acetal **(104)**. Use of the urea-hydrogen peroxide complex together with (CF₃CO₂)₂O gives, however, the desired compound **(105)** as the main product, Scheme 1. Interestingly, hydroperoxides, such as *t*-butyl, *n*-butyl, *iso*-amyl, *t*-amyl, *s*-octyl and cumene hydroperoxide are markedly stabilised as complexes with β-cyclodextrin¹⁵⁰.



Scheme 1

Unimolecular hosts such as the hemicarcerand **(106)** are also promising for the storage of reactive guests, both in the solid state and in solution¹⁵¹. Cram¹⁵¹ describes the storage of the notoriously unstable reagent diazomethane within the cavity of the protecting container **(106)**. After standing at 25°C in CDCl₃ for 1 hour, **(106)**·CH₂N₂ liberates 15% of its CH₂N₂; and after seven months in the dark solid loses 85% of its guest. Of great interest also is the containment of the very reactive guest cyclobutadiene in **(106)**, in solution, which allows further reactions to be carried out. For example, when gaseous O₂ is bubbled through the solution, the complexed *cis*-dialdehyde **(106)**·(Z)-CHOCH=CHCHO is formed¹⁵¹. CHOCH=CHCHO is formed¹⁵¹.



(106)

4.2.2 Use of Inorganic Host Lattices for Reagent Containment or Support

4.2.2.1 Zeolites, Clays, Graphite and Other Solid Supports

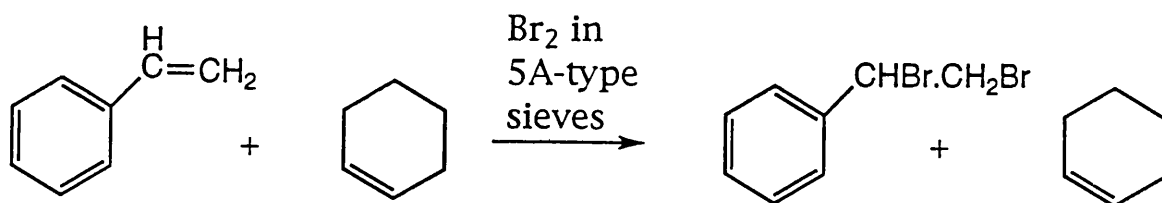
Zeolites¹⁵², crystalline aluminosilicates with voids corresponding to 20-50% of the total volume, are potentially very useful in the area of chemical storage. The range of channel and cavity topologies encountered in such systems confers the ability to include a wide range of synthetically useful molecules, for example¹⁵² NH_3 , O_2 and H_2S .

Linde A-type zeolites, especially those containing Cs^+ and Na^+ as exchangeable cations, have been used for storage¹⁵³ of H_2 . Cs_3Na_9 A-type zeolite exhibits the best incorporation of H_2 ; this corresponds to complete Cs^+ occupation of the II sites which blocks off the 8-ring apertures leading to H_2 encapsulation in the α -cages. The possible storage of radioactive ^{85}Kr in H-mordenite has also been studied¹⁵⁴.

Zeolites can also be used as solid supports for reagents. In general, solid-supported reagents^{155,156} often possess one or more of the following attributes :

1. Restricted diffusion of the reaction partners
2. Microenvironments of differing polarity, and with acidic or basic sites
3. Enzyme-like pockets to bind the substrate
4. Activation or stabilisation of the reagents
5. Ease of work-up by immobilisation of by-products, or of toxic chemicals

Advantages of solid-supported reagents^{155,156} are: the avoidance of aqueous work-up and extraction steps; and avoidance of highly toxic solvents, such as hexamethylphosphoric triamide (HMPA), in procedures currently used. Zeolites have been used to control the regioselectivity of reactions. An elegant example is the use of 5A-type molecular sieves saturated with Br₂ as a selective brominating agent¹⁵⁷. This is illustrated in Scheme 2, where this reagent only brominates the side chain of styrene, reflecting the size of the pore openings (*ca.* 4.2Å) which are too small to allow the cyclohexene to react with the encapsulated Br₂.



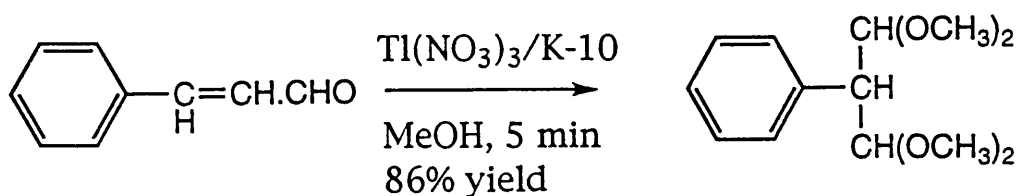
Scheme 2

The 2,4,6-triphenylpyrylium cation imprisoned inside zeolite Y has been used as a photosensitiser in the isomerisation of *cis*-stilbene to *trans*-stilbene¹⁵⁸. This reaction is not perturbed by the presence of O₂, in contrast to the extensive photooxygenation observed under homogeneous conditions.

KMnO₄-impregnated Linde 13X sieves¹⁵⁹ allows the oxidising agent to be used in organic solvents, for example benzene.

Clays, graphite, activated carbon, silica and alumina can all be used as solid supports for reagents¹⁶⁰. Here, only a few illustrative examples will be given. Copper(II) nitrate and iron(III) nitrate supported on K-10 clay, known as "claycop" and "clayfen" respectively, have been used in a variety of synthetic reactions^{161,162}. Although "clayfen" loses its activity after a few hours, "claycop" does not decompose even after storage for one month. Examples of the use of these reagents are: oxidation of alcohols; hydrolytic cleavage of thioacetals; synthesis of azides and imino phosphoranes; aromatisation of 1,4-dihydropyridines; and regioselective nitration of phenols.

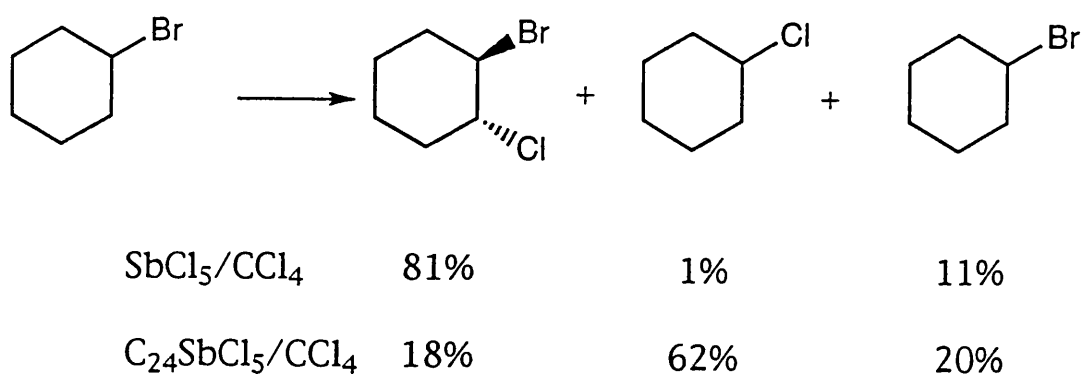
Tl(NO₃)₃/K-10 reagent has been used to carry out highly selective oxidative rearrangements¹⁶³. Thus treatment of cinnamaldehyde with this supported reagent in methanol results in rapid formation, in high yield, of phenylmalondialdehyde tetramethylacetal (107) (Scheme 3); use of Tl(NO₃)₃ in methanol, on the other hand, gives a complex mixture of products and is of no synthetic utility.



Scheme 3

Alumina has been used as a support for a wide range of reagents¹⁶⁰, and an example is sodium cyanide on neutral alumina¹⁶⁴ which converts certain alkyl halides, that are not substituted by free NaCN, into the corresponding nitriles. Studies into the structure¹⁶⁵ of NaCN/Al₂O₃ reagent suggests that the NaCN is evenly distributed between active and inactive sites, dependent upon pore size, and that only monolayer coverage is of practical synthetic value.

Graphite intercalates a wide range of compounds, although some of these either oxidise or reduce the graphite¹⁶⁶. A number of these intercalates can be used as valuable solid-supported reagents. The antimony pentachloride intercalate C₂₄SbCl₅, apparently considerably more stable than pure SbCl₅, significantly changes the product distribution on reaction¹⁶⁷ with cyclohexyl bromide, when compared with the free reagent, as shown in Scheme 4.



Scheme 4

Zn(BH₄)₂ supported on silica gel has been investigated for a variety of reactions¹⁶⁸⁻¹⁷⁰, including selective reduction processes, for example, selective reduction of epoxides to the less substituted alcohol. Metal sulphates and hydrogen sulphates have been used on the same support to effect facile

acylation of alcohols using esters¹⁷¹. These reagents bring about the selective acylation of diols to yield mono-esters¹⁷².

4.2.2.2 Other Inorganic Hosts

Alkali metal carbonates have been shown to store hydrogen peroxide¹⁷³. Figure 64 shows the crystal packing¹⁷⁴ in $\text{Na}_2\text{CO}_3 \cdot 1.5\text{H}_2\text{O}_2$; each carbonate oxygen atom forms one moderately strong hydrogen bond ($\text{O} \cdots \text{O}$ 2.54-2.65 Å) to a hydrogen peroxide molecule. The $\text{Na}_2\text{CO}_3 \cdot 1.5\text{H}_2\text{O}_2$ complex is used as an industrial bleaching agent. The same adduct has also been used to epoxidise alkenes¹⁷⁵, and its action has been compared with those of $\text{urea} \cdot \text{H}_2\text{O}_2$ and triphenylphosphine oxide $\cdot \text{H}_2\text{O}_2$. In the adduct¹⁷⁶ $4\text{Na}_2\text{SO}_4 \cdot \text{NaCl} \cdot 2\text{H}_2\text{O}_2$, stable up to *ca.* 160°C, the hydrogen peroxide is stored in tunnels¹⁷⁷, as shown in Fig. 65.

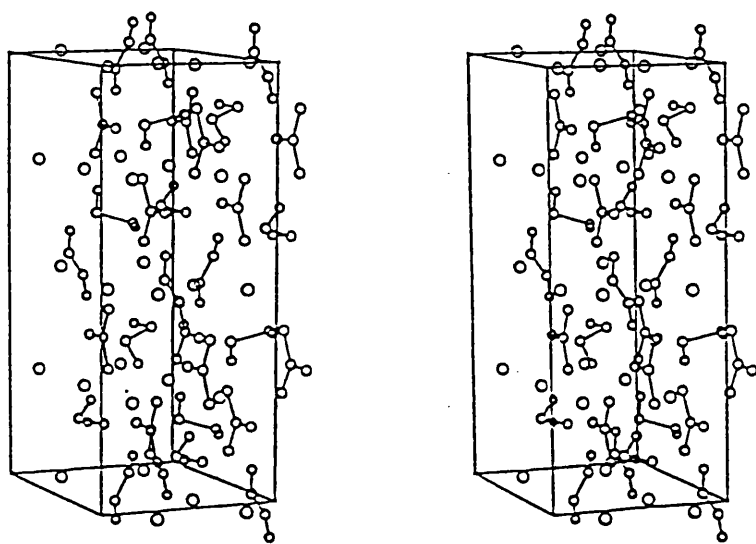


Fig. 64 A stereoview, looking approximately normal to b , illustrating the host-guest packing in the adduct $\text{Na}_2\text{CO}_3 \cdot 1.5\text{H}_2\text{O}_2$. For clarity, only one possible orientation of the disordered H_2O_2 guest is shown for each site (Ref. 174).

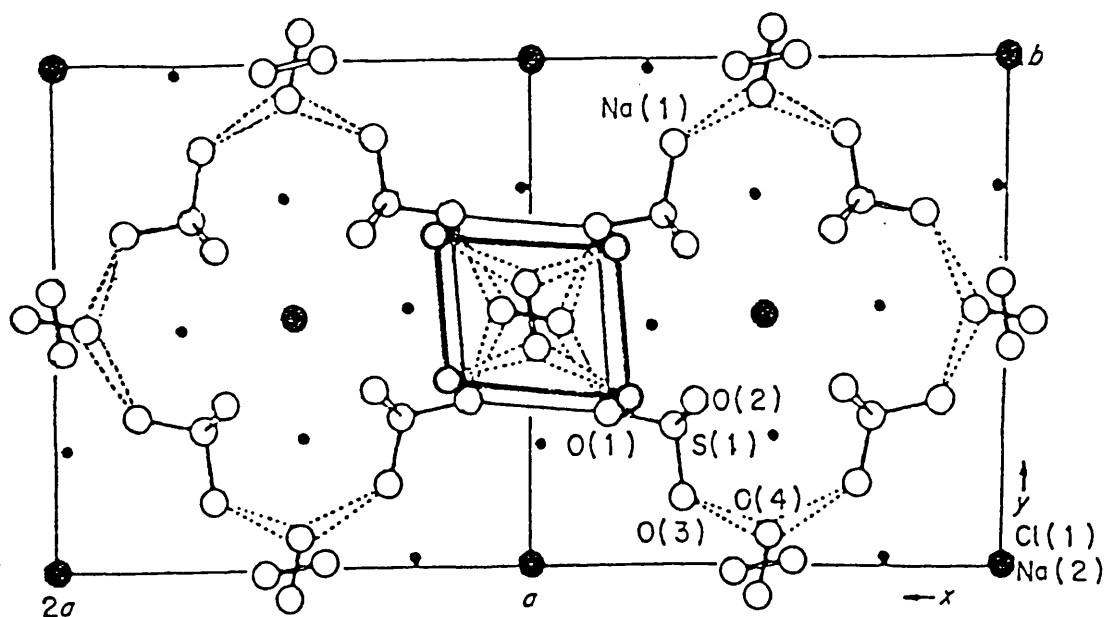


Fig. 65 A projection of the structure of $4\text{Na}_2\text{SO}_4 \cdot \text{H}_2\text{O}_2 \cdot \text{NaCl}$ on to (001) from $z = 0.0$ to $z = 0.5$. The apparent disorder of the H_2O_2 guest molecules, which lie in infinite channels along c towards the viewer, only arises because of structural determination in terms of a tetragonal cell, with $a = 10.53$, and $c = 8.42\text{\AA}$; a supercell with a and b repeat four times larger than this basis cell exists (Refs. 176, 177).

Other inorganic host lattices with potential for guest storage are $\text{Mn}[\text{Co}(\text{CN})_6]_2$, $\text{K}_2\text{Zn}_3[\text{Fe}(\text{CN})_6]_2$ and $(\text{CH}_3)_3\text{AsPdCl}_2$. These all exhibit zeolite guest-absorbing ability. $\text{Mn}[\text{Co}(\text{CN})_6]_2$ has been shown to include NH_3 , H_2S , PH_3 , MeSH and H_2S ; the rate of guest uptake is apparently governed by its ability to form hydrogen bonds¹⁷⁸. $\text{K}_2\text{Zn}_3[\text{Fe}(\text{CN})_6]_2$ absorbs CO and other gases¹⁷⁹, whilst $[\text{CH}_3)_3\text{AsPdCl}_2]_2$ absorbs H_2 into its tunnels at low temperatures¹⁸⁰.

Other inclusion complexes of interest are $(\text{NH}_4)_3\text{Mo}(\text{CNS})_6$ containing HCl , removable under vacuum¹⁸¹; $[\text{AsPh}_4]_2[\text{Mo}_2\text{Cl}_4\text{O}_4]$ also trapping HCl ¹⁸²; and $\text{Pt}_6\text{Cl}_{12}$ which includes¹⁸³ Br_2 and CS_2 .

The controlled design of new host lattices will undoubtedly lead to the ability to store a whole range of extremely reactive and valuable reagents: such effective storage media should meet the criteria set out in the Introduction. It should be emphasised that careful consideration of the geometric and chemical compatibilities of the host and guest components is crucial to the successful design of such supramolecular systems. Further crystal engineering in this existing field may confidently be expected to increase the convenience of reagent handling and also, in principle, improve regio- and stereoselectivity of synthetic reactions. Many more novel and diverse "crystal bottles" will be designed and synthesised. An attractive target, based on a saturated perfluorocarbon host lattice, may even be a supramolecular assembly capable

of storing elemental fluorine, F_2 , for potential use, for example, as a novel fluorinating agent.

TABLE

EXAMPLES OF SOLID-SUPPORTED REAGENTS

(SEE TEXT AND REF. 160)

SOLID SUPPORT	SUPPORTED REAGENT
Celite	Ag_2CO_3 , CrO_3/py
Silica	H_2O , NaOMe , CrO_2Cl_2 , AgNO_3 , MHSO_4 , M_xSO_4 , $\text{Zn}(\text{BH}_4)_2$, NR_4F , H_2CrO_4 , $[\text{PH}_3\text{P}]_4\text{Pd}$, FeCl_3
Alumina	H_2O , ROH , RSH , PhSeH , R_3N , CH_3COOH , NaBH_4 , <i>i</i> - PrOH , NaIO_4 , Tl(III)NO_3 , NaCN , Na
Graphite	AlCl_3 , SbCl_5 , SbF_5 , XeOF_4 , Br_2 , Na , K , CrO_3 , H_2SO_4 , HNO_3
Montmorillonite K-10	$\text{Fe(III)(NO}_3)_3$, $\text{Tl(III)(NO}_3)_3$, $\text{Cu(II)(NO}_3)_2$, $(\text{CH}_3\text{O})_3\text{CH}$
Kieselguhr	Cu(II)O
Activated Carbon	MnO_2 , Na , K

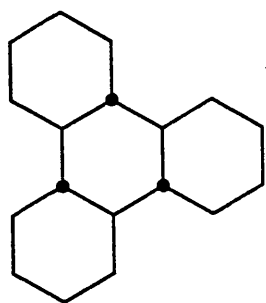
4.3 Photoreactions in Clathrates

4.3.1 Inclusion Polymerisation

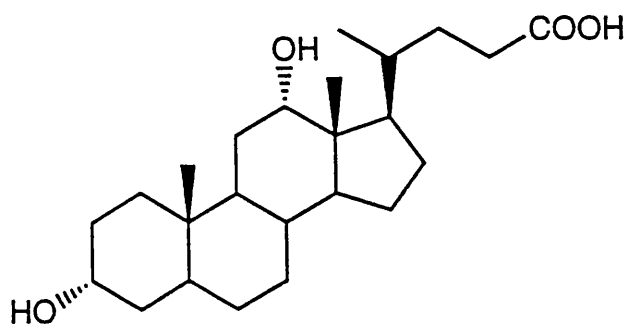
Interest in inclusion polymerisation¹⁸⁴ began to develop in the late Fifties, as an alternative method to Ziegler-Natta coordination polymerisation to obtain highly stereoregular polymers. Addition polymerisation is carried out within channel-type inclusion compounds, producing linear macromolecules with complete elimination of by-products. The reaction generally proceeds via a chain mechanism whereby a small number of initiation reactions, commonly caused by irradiation, gives rise to a large number of reactions between guest molecules (propagation reaction) and so the ratio between polymer yield and initiation reaction may reach very high values. Another advantage is that due to the macromolecular nature of the product facile separation of host and polymer guest is possible.

A number of channel inclusions have been used to study this process. The first example utilised thiourea with 2,3-dimethylbutadiene by Clasen¹⁸⁵. No initiating agent was used and polymerisation was extremely slow. Brown and White^{186,187} then continued the work using urea and thiourea with up to thirty monomers as guest molecules. In this case the polymerisation process was initiated by high energy irradiation (such as β , γ or X-ray) yielding polymers with considerable chemical and steric regularity.

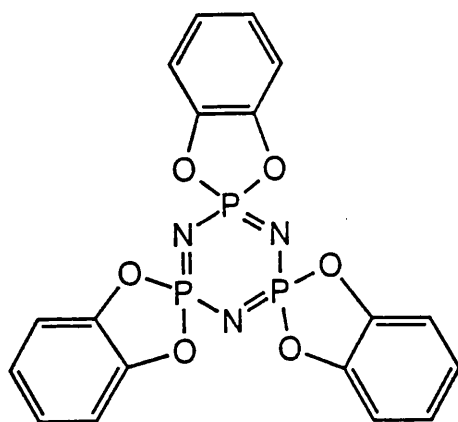
Other hosts investigated in this area are perhydrotriphenylene (4), deoxycholic acid (108) and tris(*o*-phenylenedioxy)cyclotriphosphazene (109).



(4)

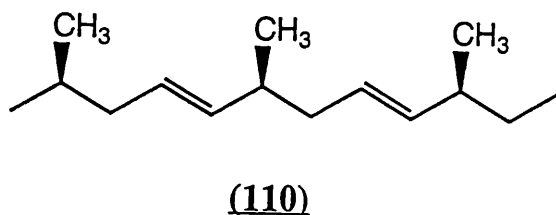


(108)



(109)

This led to different types of polymerisation depending on the size, rigidity and structure of the channel. Thiourea forms rather wide rigid channels which allows the inclusion of substituted diene monomers¹⁸⁶; urea forms narrower rigid channels suitable for smaller monomers, for example, vinyl chloride and butadiene¹⁸⁷. In contrast perhydrotriphenylene (4)²³ forms flexible channels suitable for linear and bulkier monomers. In these cases a high degree of regularity is observed, for example it has been shown that because (108) is a chiral molecule (point group D_3), then its single enantiomer^{188,189} forms a chiral crystal host lattice (space group $P6_3$) and so polymerisation of 1,3-*trans*-pentadiene in such a lattice¹⁹⁰ not only yields an isotactic polymer (110) but also an optically active one. In the case of dienes in these hosts there is always 1,4 instead of 1,2 polymerisation.



In deoxycholic acid (108) monomers of different bulkiness¹⁹¹ may be polymerised, but the resulting polymer can vary considerably in structure. Polybutadiene shows a considerable quantity (over 25%) of 1,2 units next to 1,4 units whilst poly-2,3-dimethylbutadiene is described as a highly regular 1,4-*trans* polymer¹⁹².

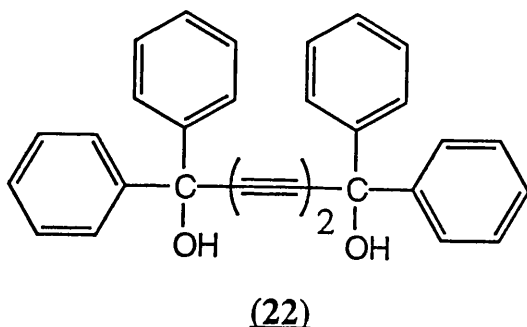
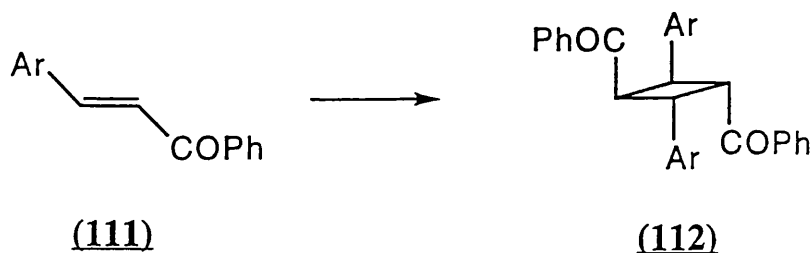
A detailed structural analysis of (108) inclusion compounds has shown that in certain cases the guest molecules are not arranged homogeneously inside the channels¹⁹³. Various arrangements or conformations of the included molecules might be responsible for the different degree of regularity. It is worth noting that the constitutional regularity of polybutadiene appears to be strongly influenced by the presence of inert additives in the channels. The addition of, say, acetone makes it possible to obtain pure or nearly pure polymers having 1,4 structure. The influence of these compounds might well be linked to the already known ability of (108) to include two different guests in its structure^{191,193,194}.

Tris(*o*-phenylenedioxy)cyclotriphosphazene (109)¹⁹⁵ has channels similar in size to that of urea, however it forms inclusion compounds with the monomer¹⁹⁶ much faster and more easily than urea and so presents considerable advantages.

Although it has not yet reached the state that it can be used for large scale preparation of polymers, inclusion polymerisation is still of great interest especially because of the high degree of regularity it can impart on the polymer formed.

4.3.2 Other Photoreactions

Chalcone (111) when irradiated in solution or in the solid state gives a mixture of (111), its *cis* isomer¹⁹⁷ and all possible stereoisomeric photodimers (112)⁹⁸.



However, irradiation of a 1:2 complex of (22) and (111) in the solid state gives the *syn* head-to-tail dimer (112) in 90% yield^{199,200}. The X-ray structure²⁰¹ of the 1:2 complex (Fig. 66) explains why such control happens. Two molecules are packed close together in the arrangement which gives the *syn* head to tail dimer but not the other isomers. The double bonds are parallel and the distance is short enough (3.862Å) to allow them to react easily (in order for them to be able to react Schmidts rule²⁰² states that the distance should be no longer than 4.2Å) (Fig. 67).

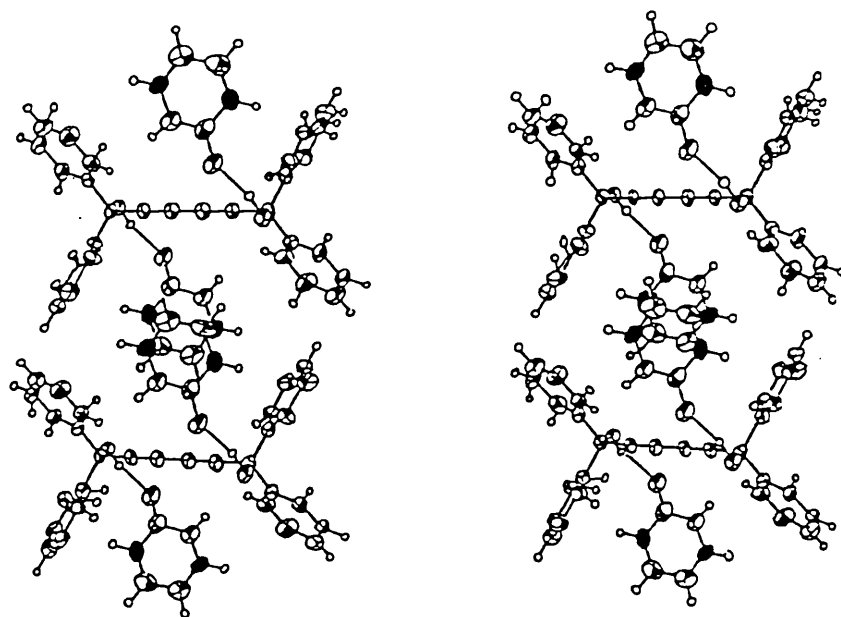


Fig.66 A stereoscopic view of the 1:2 inclusion compound of (22) and (111)

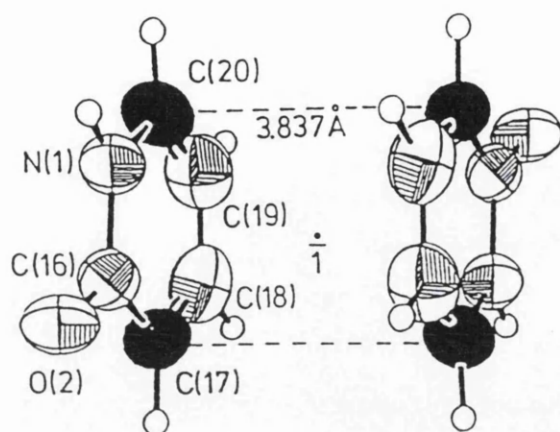
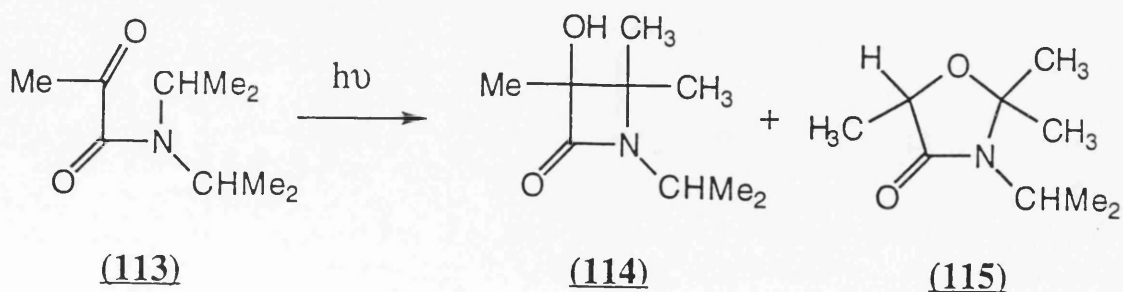
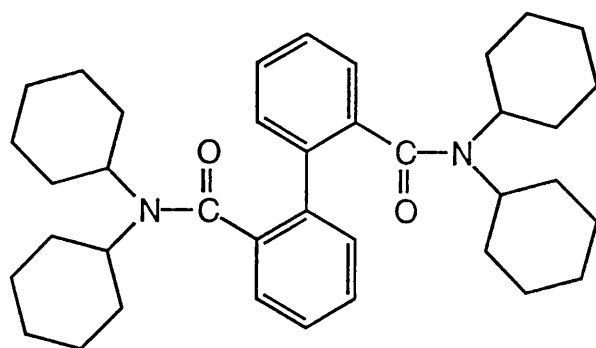


Fig. 67 The mutual relationship and geometrical parameters of the reacting centres of the pair of (111) molecules.

Photocyclisation of α -oxoamides (113) has been used to synthesise β -lactams, however, this gives a complex mixture of *cis* and *trans* isomers of β -lactams (114) and oxazolidin-4-ones (115)^{203,204}.

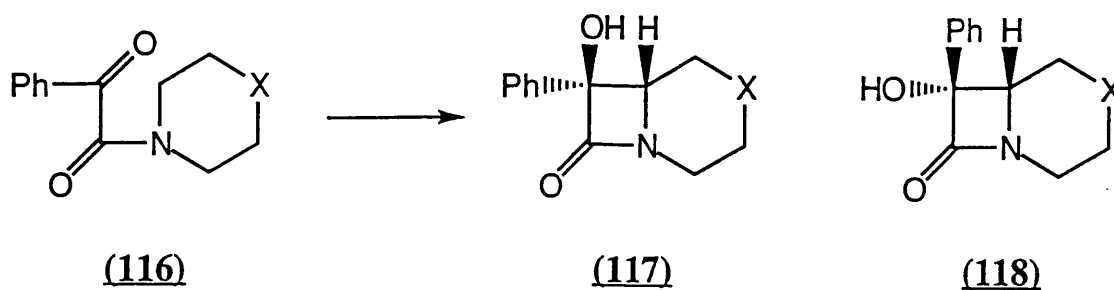


(38) forms 1:1 clathrates with a variety of α -oxoamides and upon irradiation of the complex the β -lactam is formed exclusively²⁰⁵.



(38)

Although irradiation of (116) in solution gives a mixture of *cis* (117) and *trans* β -lactam (118)^{203,204} irradiation of the 1:1 complex of (116) and (38) in the solid state gives the *cis* isomer (117) exclusively²⁰⁶.



Toda then took this a stage further and utilised chiral hosts to produce enantioselective photoreactions. He irradiated the 1:1 inclusion compound of (113) and (-)-(30) in the solid state for 8 hours to give (-)-(114) in 90% yield and 100% e.e.^{205,207}.

The X-ray structure of the complex shows that the symmetrical, and therefore achiral, molecules of (113) is arranged unsymmetrically, and therefore chirally, by twisting around the bond between the two carbonyl groups²⁰⁷. This can be seen in Fig. 68 and 69.

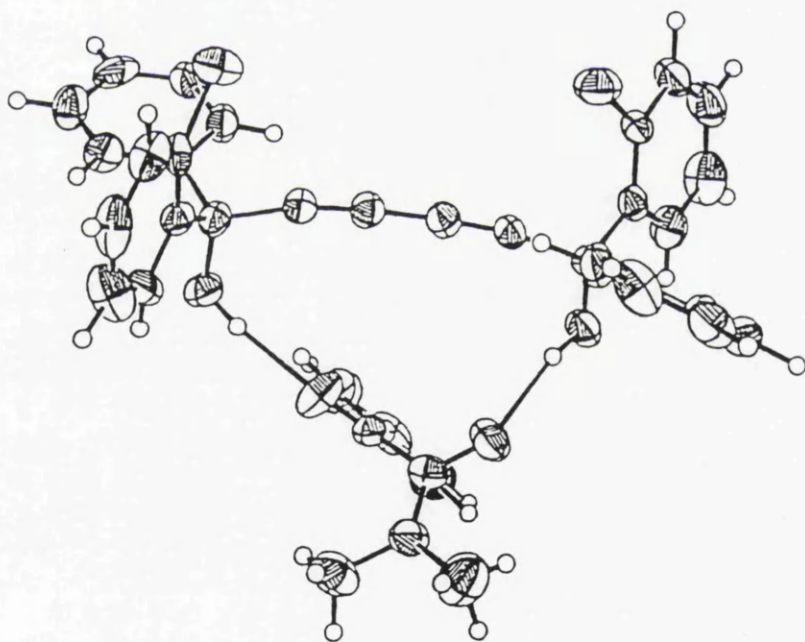


Fig. 68 Stereoscopic view of the 1:1 inclusion compound of (-)-(30) and (113).

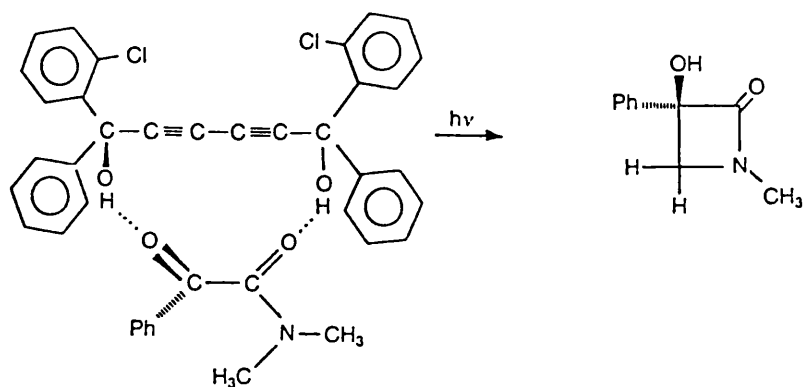


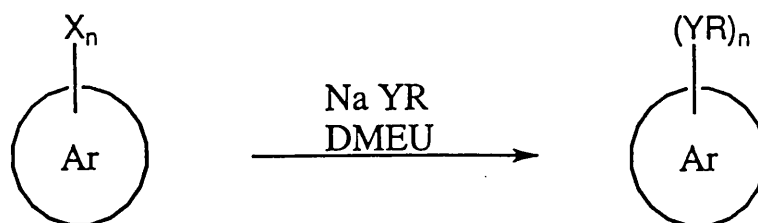
Fig. 69 A schematic illustration of the enantioselective photocyclisation of (113) in its inclusion compound with $(-)$ -(130).

5. RESULTS AND DISCUSSION

As discussed in the previous chapters, the hexa-host analogy and the use of trigonal symmetry have played an important role in host design. 2-fold symmetry is also prevalent in host molecules, such as binaphthol, acetylenic diols and Bishop's diols.

In this chapter novel persubstituted cores will be discussed with respect to the design of new hexa-host derivatives.

The general reaction for the synthesis of these new hosts involves the persubstitution of perhaloaromatic compounds, in DMEU, using thiolate or phenolate anions (Scheme 5).



Ar : Aromatic Core
X : F, Cl, Br
Y : O, S

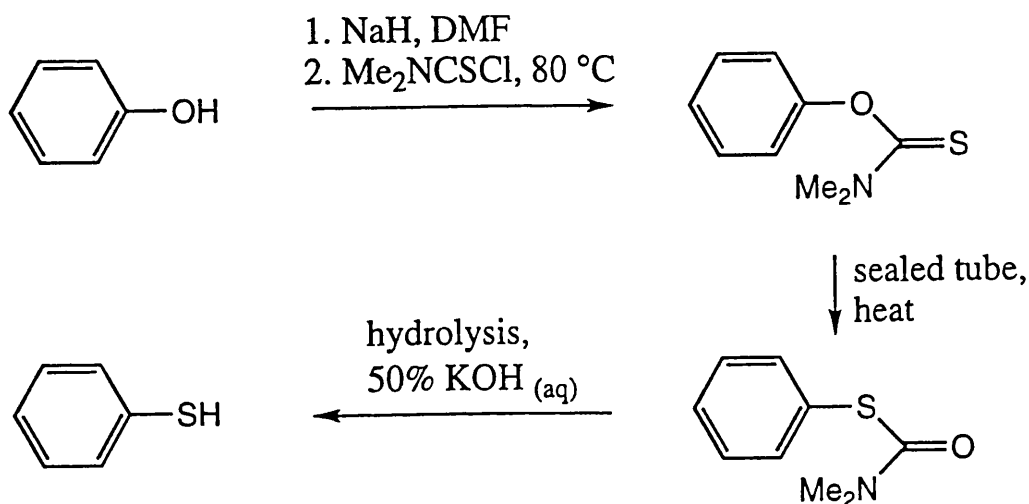
Scheme 5

With this in mind, a variety of the methods were used to synthesise non-commercially available thiols and phenols.

5.1 Synthesis of thiols and phenols

5.1.1 Aromatic thiols

To synthesise different aromatic thiols the synthetic method of Newman and Karnes²⁰⁸ was used (Scheme 6).

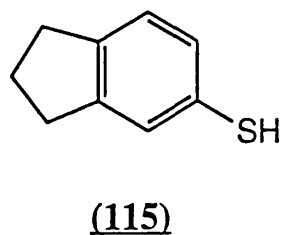
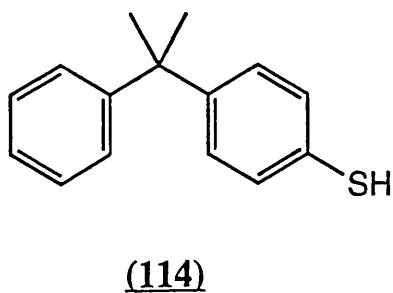


Scheme 6

The phenoxide salt, formed by reaction of the phenol with NaH, was reacted with *N,N*-dimethylthiocarbonylchloride. By simple nucleophilic displacement the *O*-aryl dimethylthiocarbamate is obtained and this was then rearranged to the more stable *S*-aryl dimethylthiocarbamate in a vacuum-sealed pyrolysis tube. Care has to be taken here as moisture in the tube can lead to hydrolysis of the *O*-aryl dimethylthiocarbamate under the rearrangement conditions. The *S*-aryl dimethylthiocarbamate is then

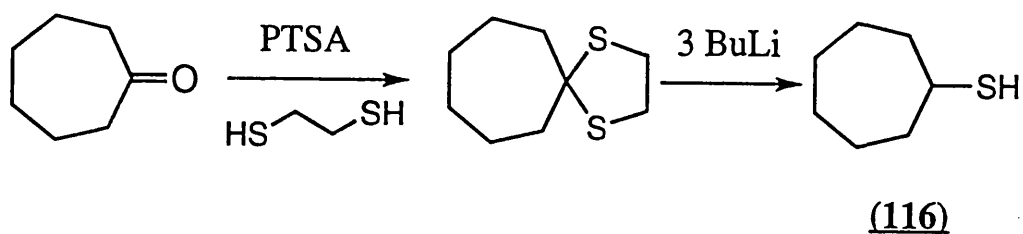
hydrolysed under an inert atmosphere of nitrogen (to avoid disulphide formation) and the thiol subsequently isolated.

Both *p*-cumylphenylthiol (**114**) and 5-indanethiol (**115**) were synthesised in this way.



5.1.2 Cycloalkylthiols

Cycloheptanethiol (**116**) was prepared by the method of Wilson and Georgiadis^{209,210} (Scheme 7).



Scheme 7

Cycloheptanone (116) was reacted with ethanedithiol in the presence of a catalytic amount of acid, in a Dean-Stark apparatus to yield the dithioketal which is then reacted with 3 equivalents of BuLi to give thiol (116).

The reaction is believed to go through cycloheptanethione which is reduced²¹¹ to the thiol by β -hydrogen transfer from the BuLi (Fig. 70).

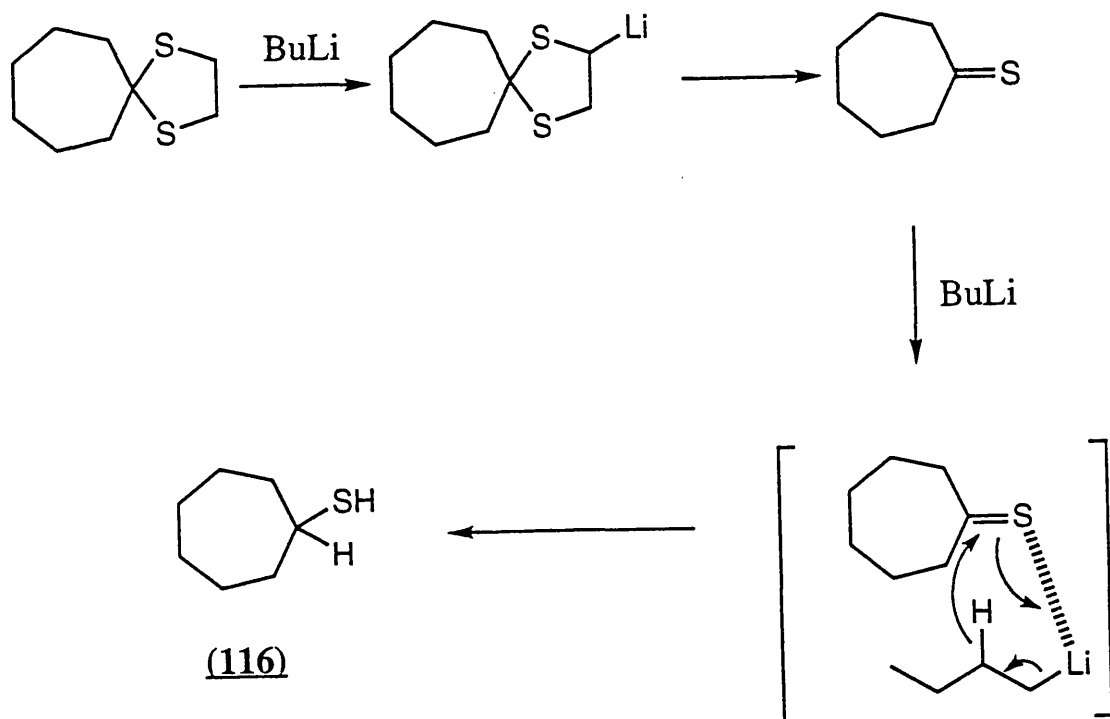
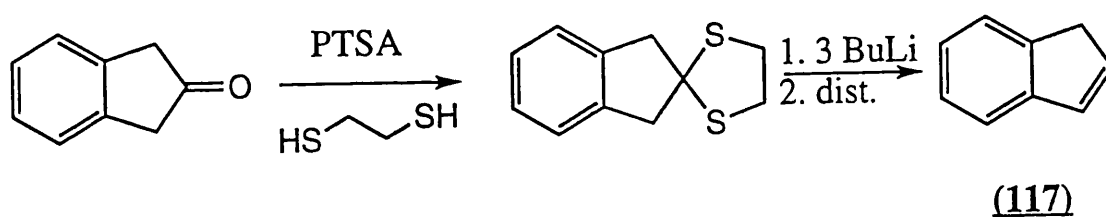


Fig. 70 Proposed mechanism for the formation of (116)

The reaction was also tried starting with indan-2-one (Scheme 8); however under the reaction conditions , and purification by reduced-pressure distillation, a large amount of indene (117), observed by ^1H NMR, was produced in the final step.

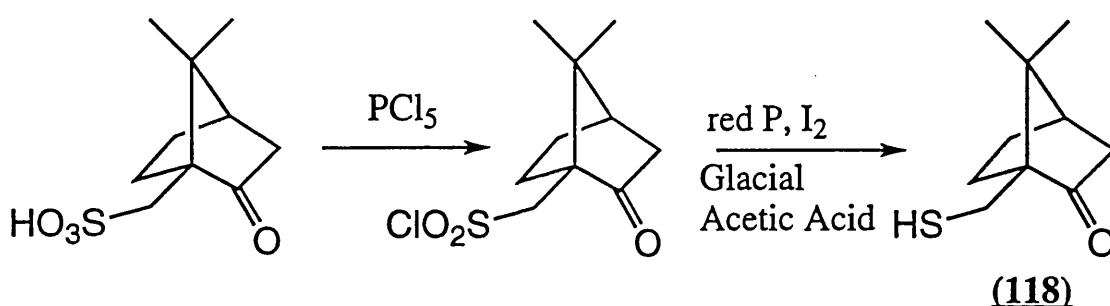


Scheme 8

Although not tried, it is believed that extraction into aqueous KOH, and subsequent acidification would give the thiol in reasonable purity^{209,210}.

5.1.3. 10-(S)-Mercaptocamphor (118)

This was prepared ²¹³ by utilising a known method for the synthesis of aromatic thiols. Starting from the camphorsulphonic acid, the acid chloride was prepared with PCl_5 and then the isolated dried camphor-10-sulphonylchloride was reduced to the thiol (118) with red phosphorous, iodine and glacial acetic acid, which was purified by steam distillation (Scheme 9).

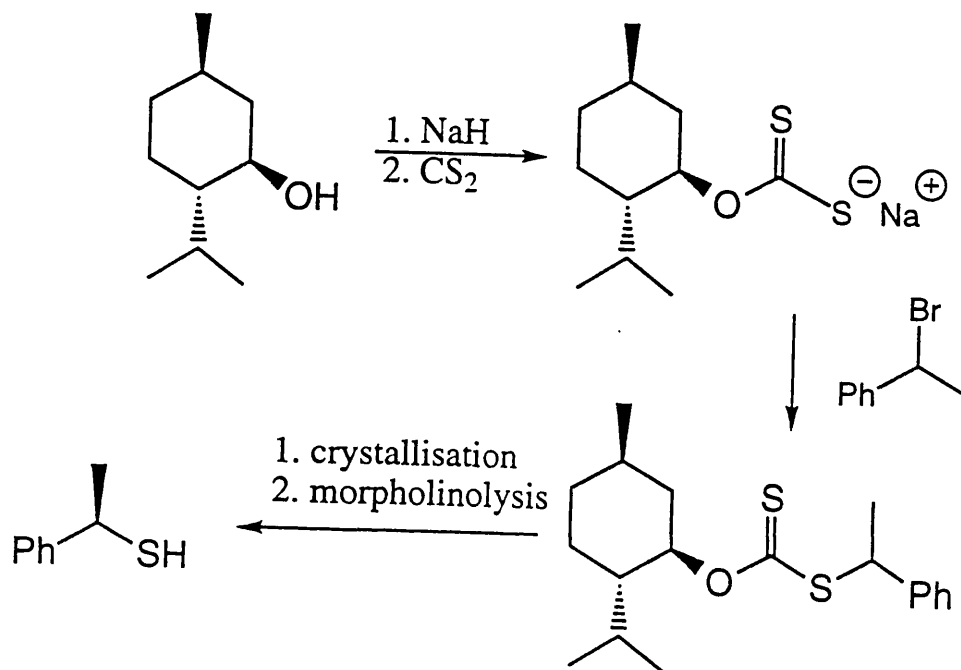


Scheme 9

The formation of HI , from the iodine in the presence of acid, is believed to be the reducing agent.

5.1.4 (+)-1-Phenylethylthiol (**119**)

This chiral thiol was synthesised by the method of Isola and co-workers²¹⁵ (Scheme 10).

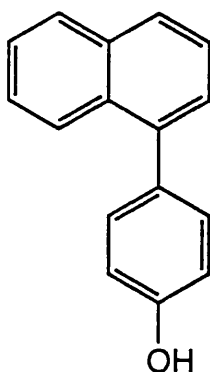


Scheme 10

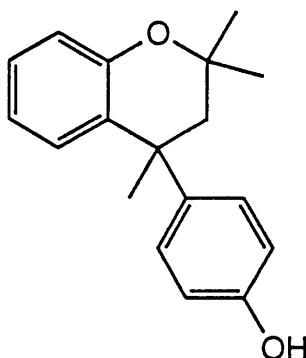
The (-)-sodium-*O*-menthlyldithiocarbamate, prepared from (-)-menthol and carbon disulphide was reacted with the racemic bromide to give a mixture of two diastereoisomers which were separated by fractional crystallisation. The resulting optically active xanthate ester was then decomposed using morpholine to obtain the chiral thiol (+)-1-phenylethylthiol (**119**).

5.1.5 *p*-Naphthylphenol (120)

This phenol was synthesised because of its similarity in shape to the well-known phenolic host Dianin's compound (6).

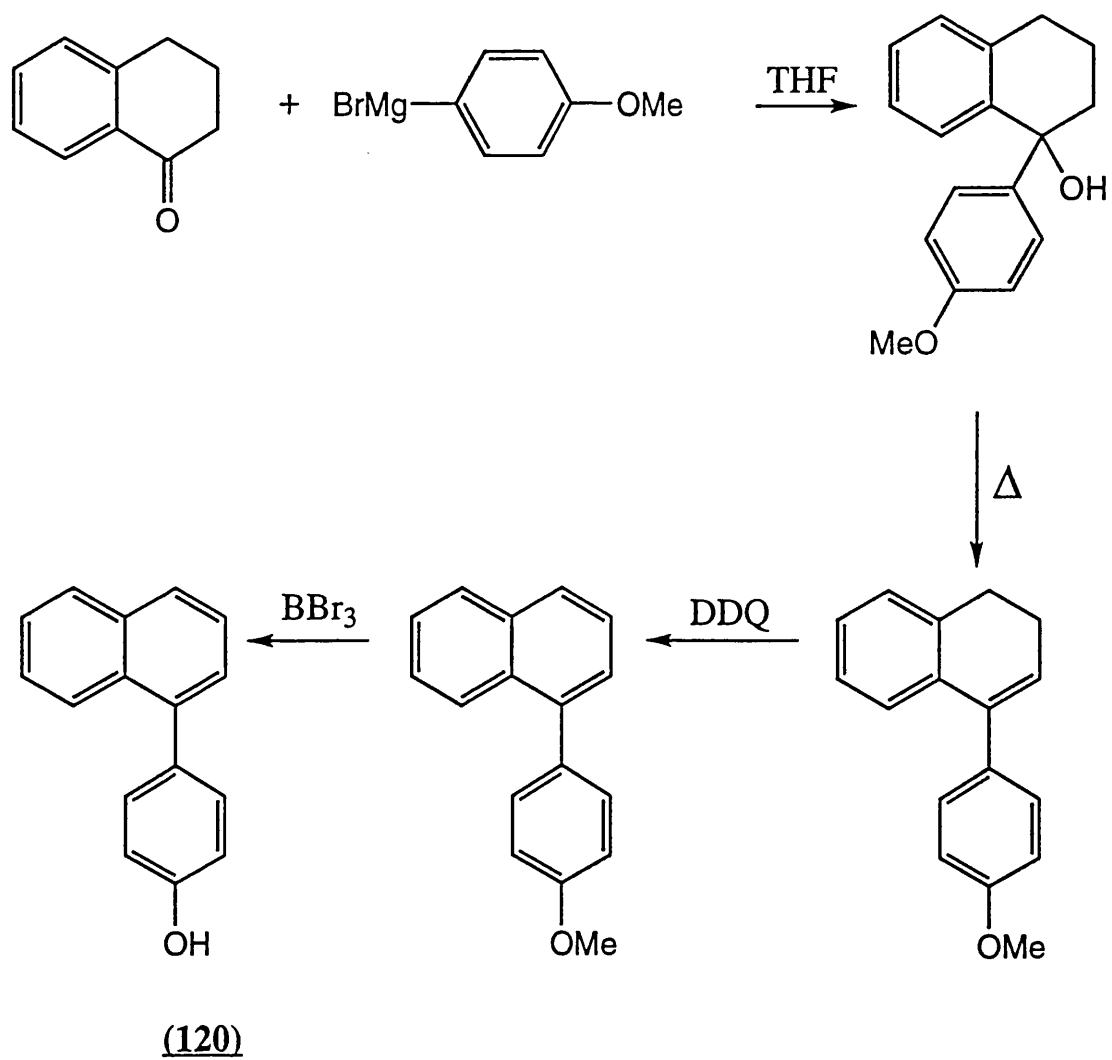


(120)



(6)

It was prepared (Scheme 11) by reacting α -tetralone with the Grignard reagent from *p*-methoxybromobenzene which under distillation dehydrates to give 1-(*p*-methoxyphenyl)-3,4-dihydronaphthalene. This was then dehydrogenated using 2,3-dichloro-5,6-dicyanoquinone (DDQ) and finally demethylated using boron tribromide (BBr_3).

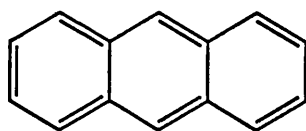


Scheme 11

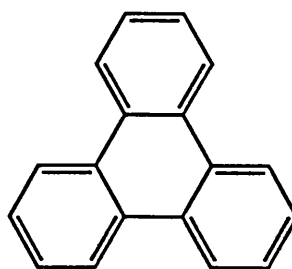
5.2 Fused Aromatic-Core Hosts

As has already been mentioned, a number of different persubstituted core units have already been investigated as potential host units. This includes the fused aromatic cores such as naphthalene⁹⁵⁻⁹⁷, phenanthrene⁹⁸, acenaphthalene⁹⁷ and coronene⁹⁷. Of these only the naphthalene and coronene showed any propensity to form clathrates, suggesting that a symmetry axis running perpendicular to the aromatic core is important.

It was then decided to investigate two other fused aromatic core units, namely anthracene (121), and triphenylene (122).



(121)



(122)

5.2.1 Anthracene

The anthracene core has the potential of adopting a C_2 axis of symmetry perpendicular to the core unit suggesting that it was likely that this could be a source of novel inclusion compounds.

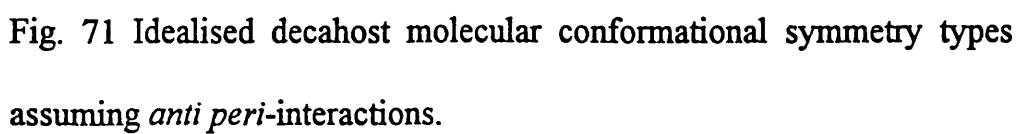
There are 14 possible conformers that a persubstituted anthracene can adopt, assuming *anti* arrangement for *peri*-related groups. The classification for these conformers is based primarily on symmetry, assuming achiral legs. The greatest weight is placed on proper rotation axes, in the order C_{2h} , C_{2v} , C_2 , C_s , C_i , C_1 . Secondary ranking was based on the degree of leg alternation, the most with the higher priority. The final criterion is based on the symmetry of the central 10 carbon atoms with symmetry as before i.e. C_{2h} over C_{2v} .

Under these criteria the 14 types (Fig. 71) of conformers are: Type I, ababababab (C_{2h}); Type II, aabbabbaab (C_{2h}); Type III, abbababbab (C_{2v}); Type IV, aaaabaaaab (C_{2v}); Type V, abababbaab (C_2); Type VI, abaababaab (C_2); Type VII, abaabaabab (C_s); Type VIII, aaababaaaab (C_s); Type IX, abbabaaaab (C_s); Type X, abbbabaaaab (C_i); Type XI, abababaaaab (C_1); Type XII, abbabaabab (C_1); Type XIII, aabbabaaaab (C_1); Type XIV, abaabaaaab (C_1), where

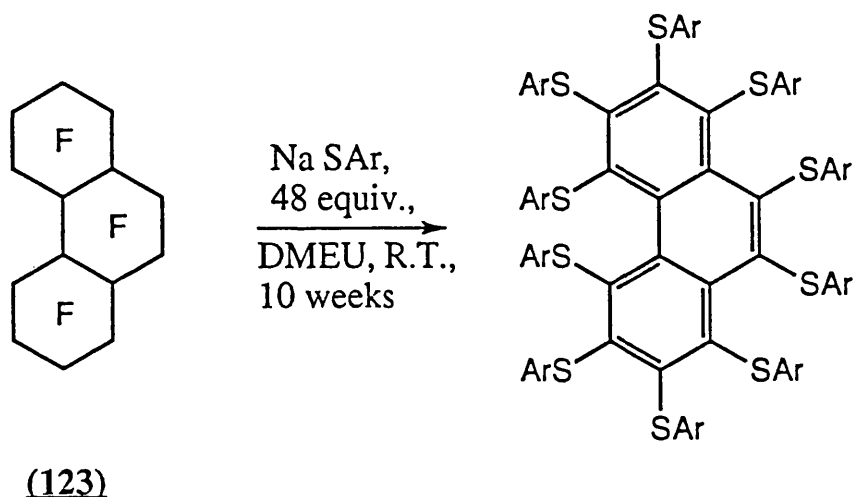
a and b denote the leg projections relatively above or below the central anthracene core.

It was decided to synthesise these persubstituted anthracenes by extending an interesting reaction discovered by MacNicol and co-workers.

Prior to 1986, saturated fluorocarbons were regarded as almost totally inert materials, reactions were found to occur only under very extreme conditions. This property led to many applications ranging from non-stick surfaces to blood substitutes²¹⁶.

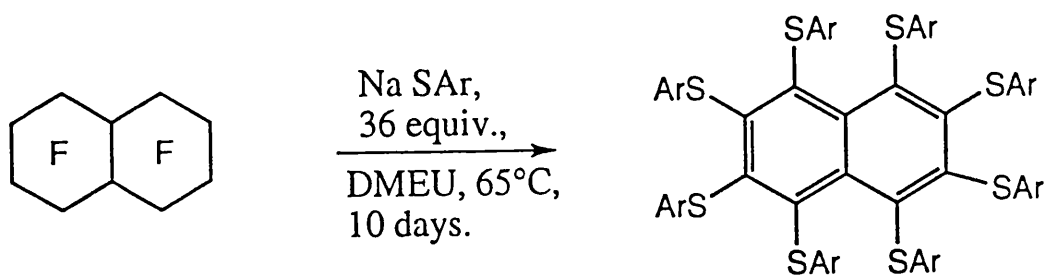


The inertness was more-or-less accepted until MacNicol and McGregor in 1986 found by chance that perfluoroperhydrophenanthrene **(123)** was completely, albeit slowly, aromatised and persubstituted²¹⁷ by arenethiolate nucleophiles in DMEU (Scheme 12). This discovery of novel reactivity was proved spectroscopically but no X-ray work was attempted at this time.



Scheme 12

MacNicol and Robertson then extended the study of this interesting reactivity to perfluorodecalin **(124)**, reasoning that aromatisation and substitution should occur to produce a spider-host by a very novel route²¹⁸. Experimental results backed by a single-crystal X-ray analysis, proved this to be the case. Optimal reaction conditions are shown below (Scheme 13).



(124)

Scheme 13

Limitations to the reaction were noted from a more extensive investigation²¹⁹: (a) The fluorocarbon must possess a tertiary centre otherwise no reaction will occur, for example perfluorocyclohexane was found to be completely inert; and (b) the temperature must not be raised above 70°C, in order to prevent decomposition of the product by side-chain cleavage.

To explain this novel reactivity, three reaction mechanisms were considered (Fig. 72). The initial stage, proceeding to a possible intermediate, could occur by three distinct routes:-

- (a) S_N2 attack at carbon, $S_N2(C)$
- (b) S_N2 attack at fluorine, $S_N2(F)$
- (c) Single electron transfer, S.E.T.

Normally, fluorinated systems are resistant to $S_N2(C)$ attack; displacement of fluoride from CF_3 or CF_2H by attack at carbon with an external nucleophile has not been unambiguously established. Similarly, no examples exist for direct $S_N2(F)$ attack when fluorine is attached

directly to carbon in any fluorinated molecule. The most likely mechanism is of the S.E.T. type, favoured particularly by the high electron affinities of cyclic saturated fluorocarbons.

Initiation of the reaction is envisaged to occur at the tertiary centre possessing the electron affinity. Two modes of electron transfer are possible leading to the intermediate bridgehead anion (Fig. 72). The mono-olefin is then formed; immediately followed by aromatisation and persubstitution, via combined addition-elimination, *ipso*-substitution and reductive reactions (Fig. 73), to produce a spider-host by a novel route.

This has now been extended by MacNicol and Downing to persubstituted acenaphthalene and coronene derivatives⁹⁷. It was therefore of interest to react perfluoroperhyroanthracene (125), in DMEU, with sodium cyclopentylthiolate; The reaction conditions being 60°C for one week in the dark, to avoid extensive leg cleavage. This gave purple crystals of decakis(cyclopentylthio)anthracene (127) in about 10% yield.

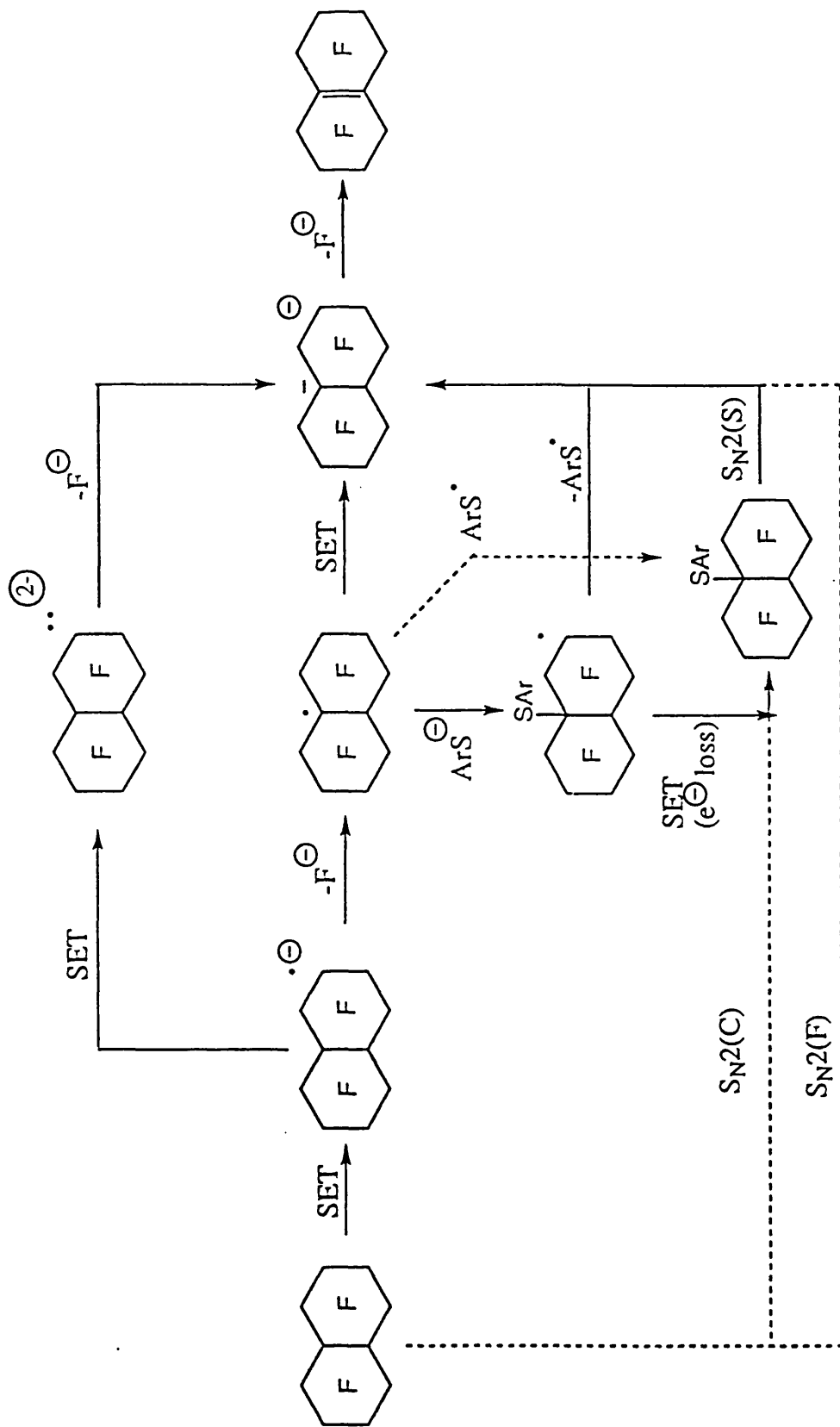


Fig.72 Novel reactivity of perfluorodecalin: alternative pathways to the proposed intermediate perfluoroalkene.

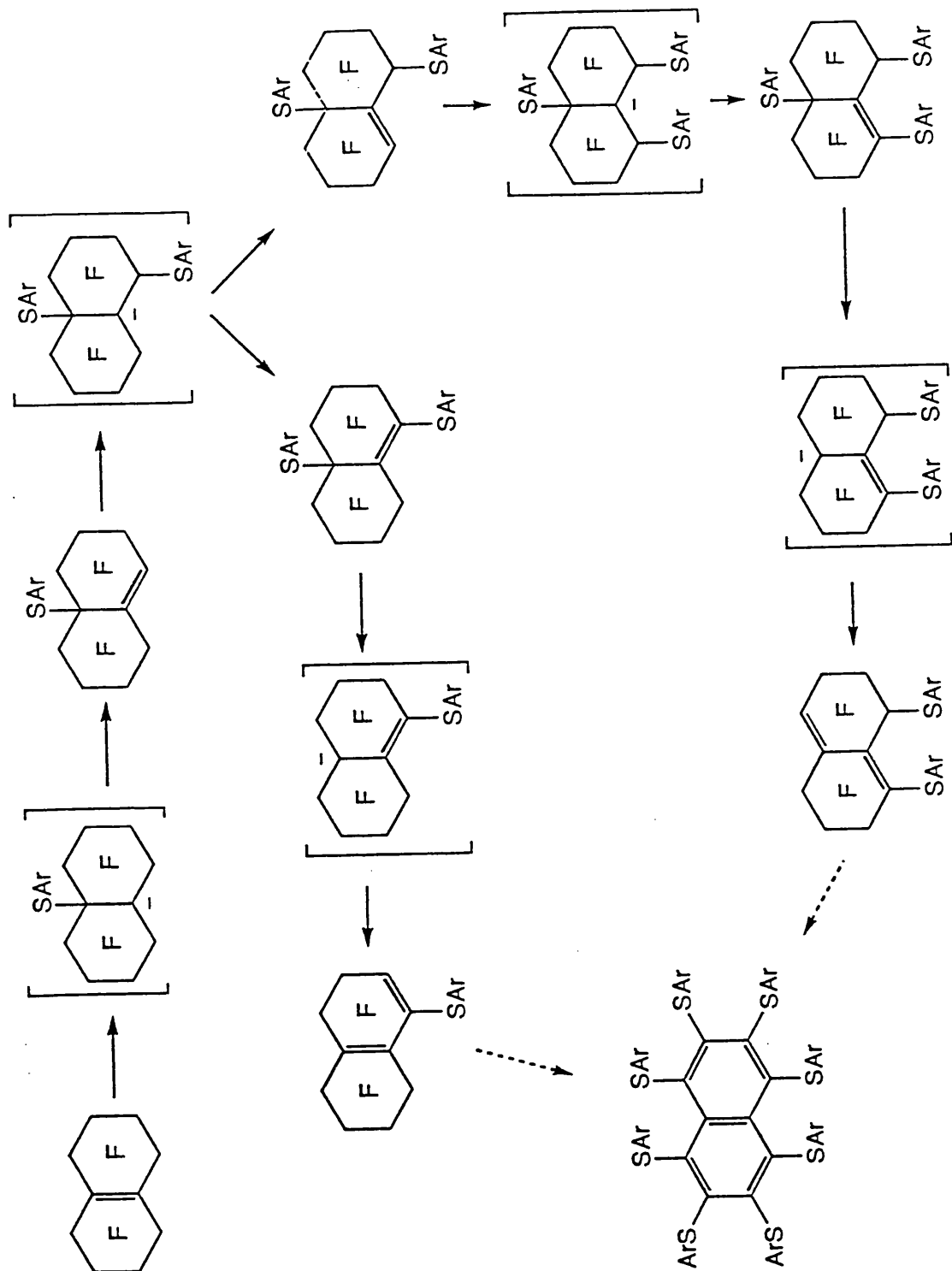
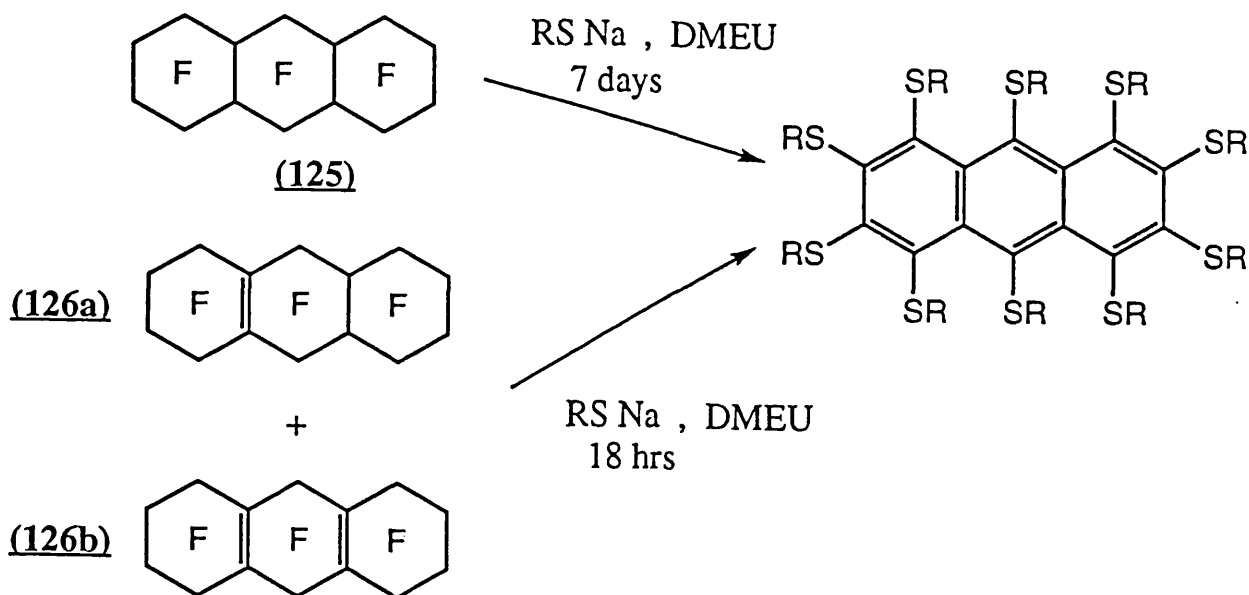
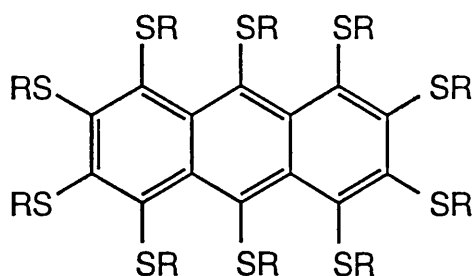


Fig. 73 Outline of some possible initial steps for the aromatisation of proposed intermediate alkene: subsequent steps (not shown) also involve combined addition-elimination, continued *ipso*-substitution, and progressive reduction.

If the mechanism were to be as proposed, synthesis of (127) should be possible, from an intermediate olefin or mixture of olefins. This was tried using a mixture of the perfluoro-olefins (126). The reaction went to completion after only one day to give (127) in about 37% yield (Scheme 14).



Scheme 14



SR	SR
<p>(127)</p>	<p>(129)</p>
<p>(128)</p>	<p>(130)</p>

Table 1. Structural formulae of persubstituted anthracenes (127)-(130).

Figs. 74 and 75 show the proposed mechanism for this reaction. The mechanism is believed to be similar to that for perfluorodecalin. The fact that the olefin reacts faster suggests that the rate determining step is the olefin formation by S.E.T. and the increase in yield is put down to a smaller reaction time and so less chance of leg cleavage. In fact if the reaction is performed, with the olefin mixture (126), without taking the precaution of excluding light then the yield drops to *ca.* 15% and an increase in leg cleavage products can be seen by TLC.

Decakis(cyclopentylthio)anthracene (127) was shown to include a wide variety of guests (Table 2).

Guest	Host:Guest Ratio	Method of Analysis(a)
1,4-dioxane	2 : 3	¹ H NMR, MA, TGA
1,4-thioxane	2 : 3	¹ H NMR
pyridine	ca. 1 : 1	¹ H NMR, TGA
toluene	ca. 1 : 1	¹ H NMR
N-methylmorpholine	1 : 1	¹ H NMR
cyclohexanone	1 : 1	TGA

(a) ¹H NMR at 200 MHz; MA - Microanalysis; TGA - Thermal Gravimetric Analysis.

Table 2. Representative inclusion compounds formed by decakis(cyclopentylthio)anthracene (127).

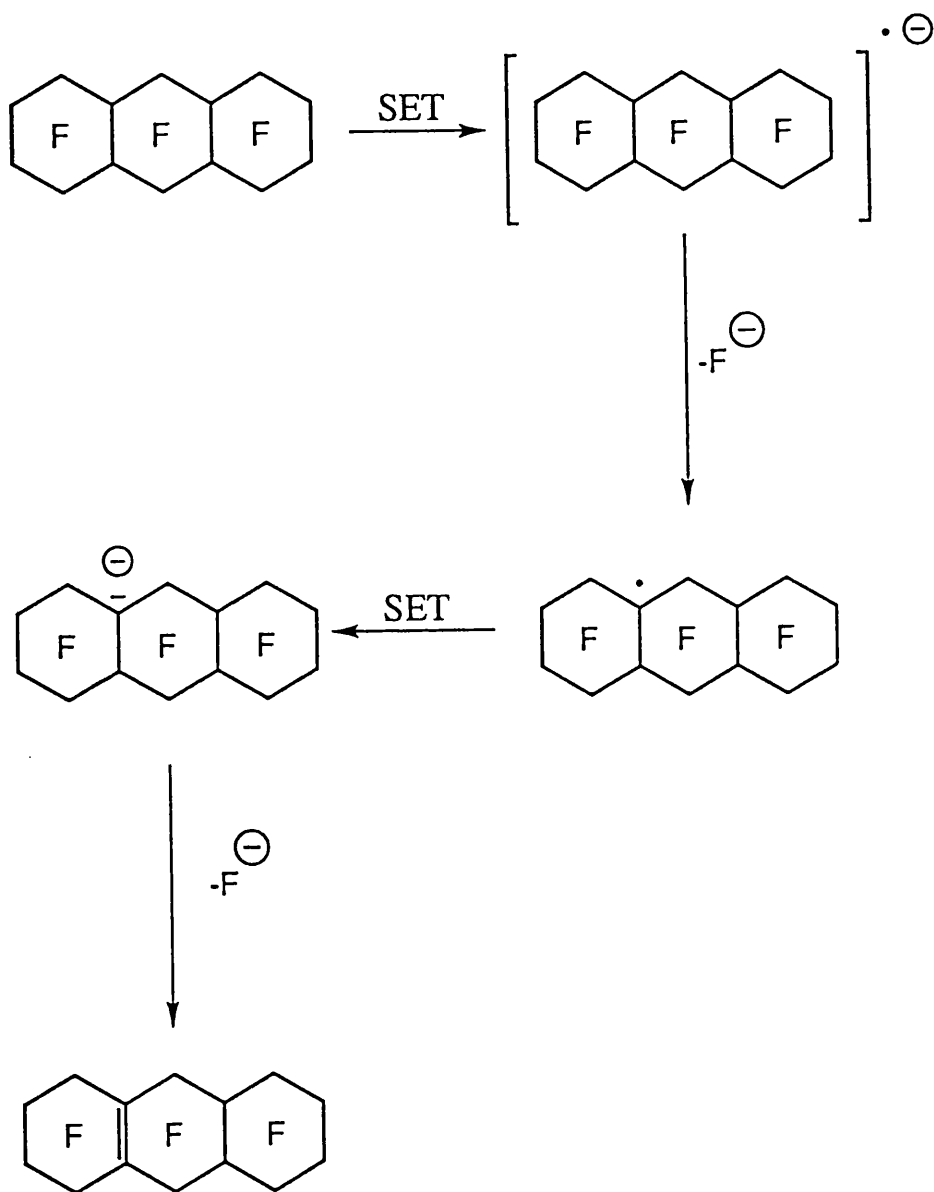


Fig. 74 Proposed mechanism for the formation of perfluoro-olefin
(126a).

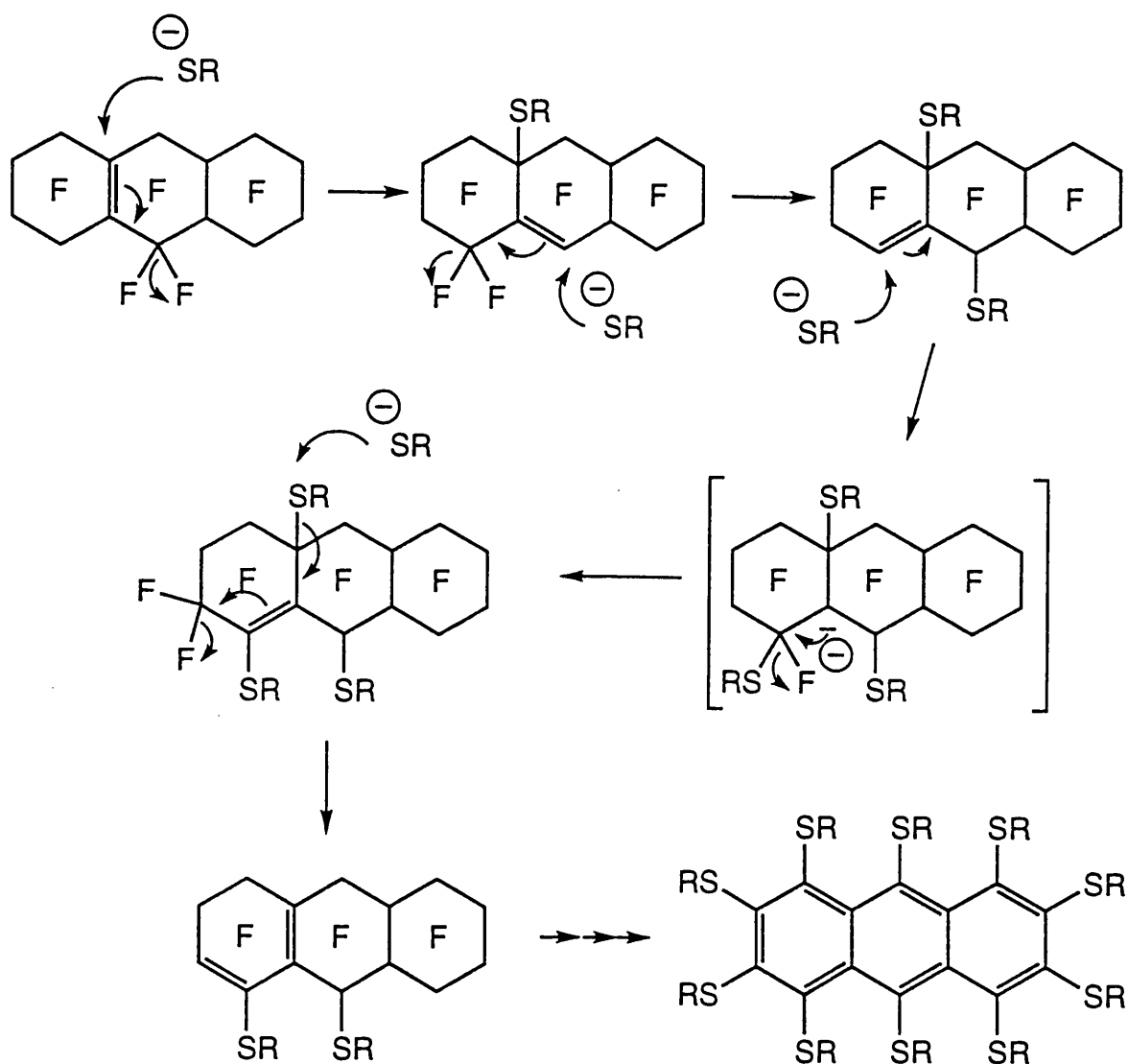


Fig. 75 Proposed mechanism for aromatisation and persubstitution of perfluoro-olefin (126a) by arenethiolate nucleophiles.

Single-crystal X-ray analysis of the 1,4-dioxane.(127) clathrate shows that the adduct is triclinic, space group $P\bar{1}$, and the unit cell contains two centrosymmetrically related host molecules. This can be seen in Fig. 76 which shows a stereoview of the clathrate. There are two distinct locations for the 1,4-dioxane guest molecules; one corresponds to a general position in the unit cell, the other a centre of inversion $\bar{1}$, half way along the a -axis. Both 1,4-dioxane guest types have a chair conformation.

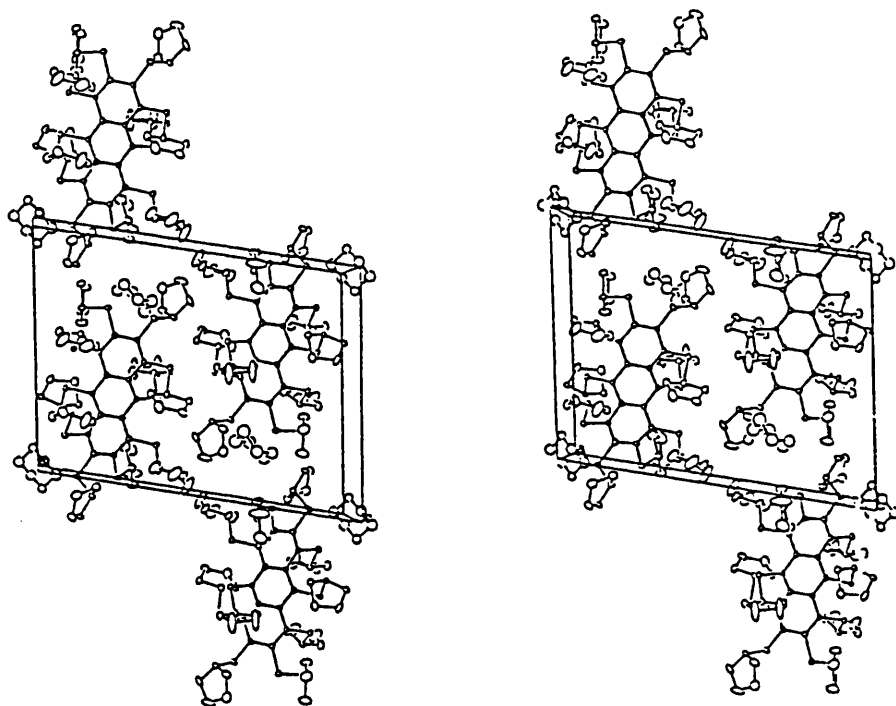


Fig. 76 A stereoview looking along the a -axis illustrating the host-guest packing in 1,4-dioxane inclusion compound of host (127).

Fig. 77 shows the conformation of the host molecule. It adopts the asymmetric Type XII conformation abbabaabab.

In marked contrast to anthracene itself, which is co-planar to within 0.01Å, the central aromatic core of **(127)** is markedly non-planar reflecting the pronounced *peri*-interactions. Interestingly, each of the three crystallographically independent six membered rings approximates quite well to a shallow twist boat conformation, as may be appreciated from the torsion angles in Fig. 78, which also gives displacements of the sulphur atoms from the mean plane of the aromatic core.

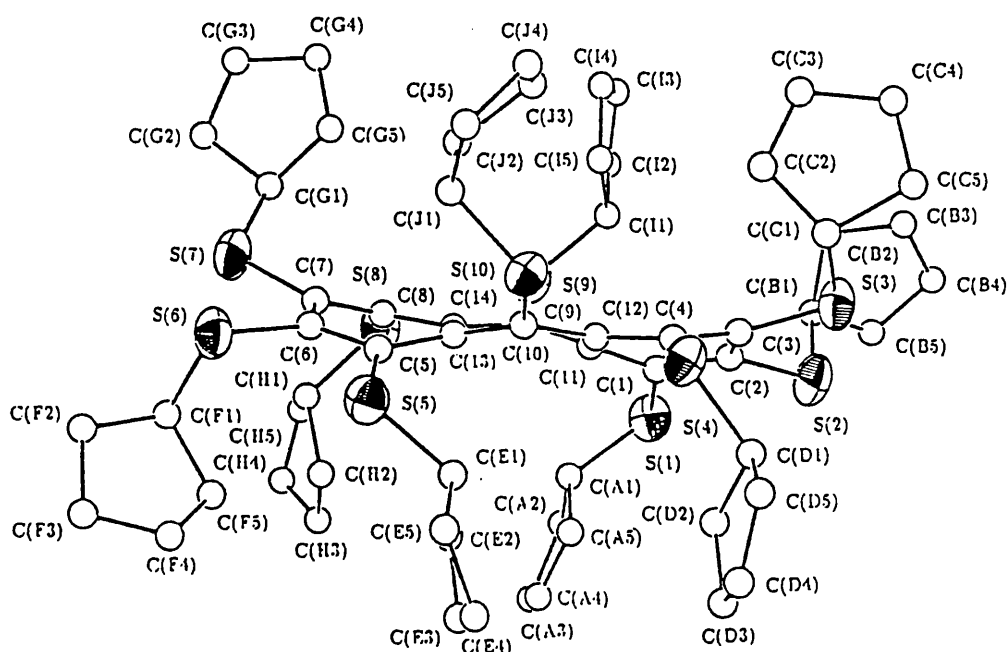


Fig. 77 A view of the molecular structure of decakis(cyclopentylthio)anthracene **(127)** in its 1,4-dioxane inclusion compound, showing the host's atomic numbering.

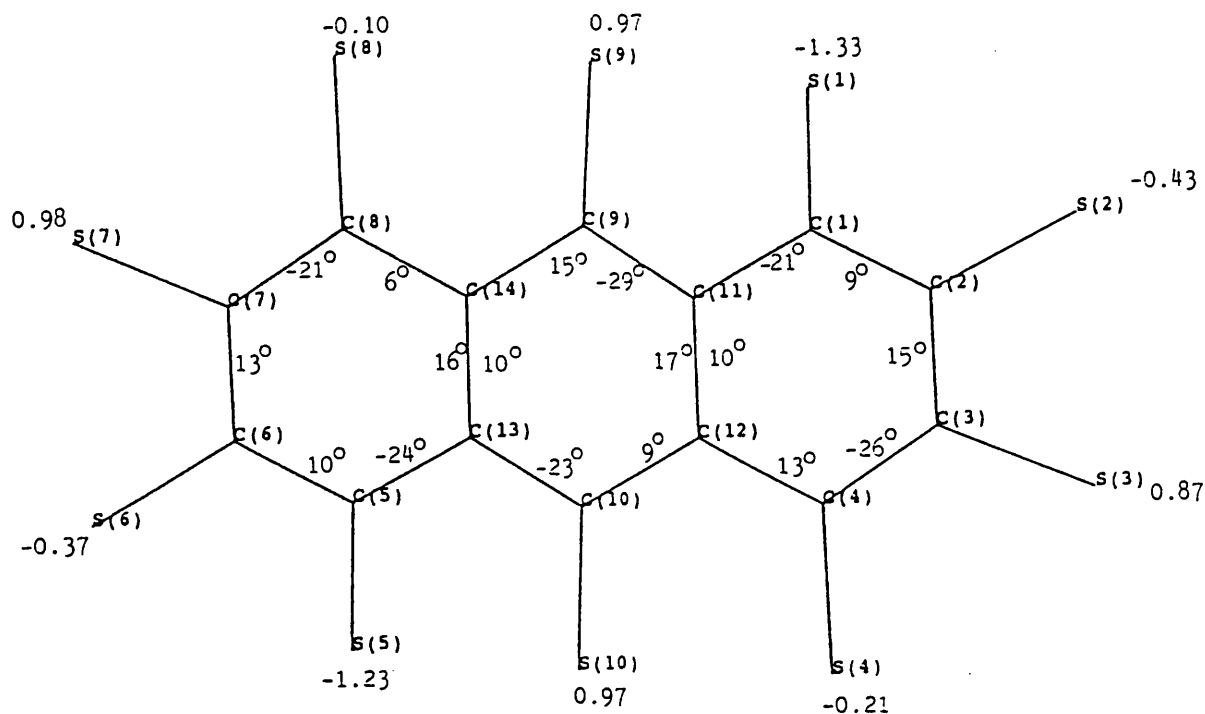


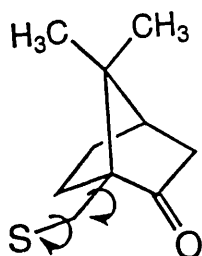
Fig. 78 Torsion angles and displacements (Å) of the sulphur atoms from the mean plane defined by atoms C(1) to C(14) inclusive, for decakis(cyclopentylthio)anthracene (127) [1,4-dioxane adduct], indicating the approximately C_2 -symmetric core. This local non-crystallographic two-fold symmetry is also apparent from displacements of related pairs of atoms from the same mean anthracene plane: C(1), C(5), -0.43, -0.42; C(2), C(6), -0.12, -0.13; C(3), C(7), 0.32, 0.30; C(4), C(8), 0.13, 0.16; C(12), C(14), 0.05, 0.02; C(10), C(9), 0.16, 0.18; C(13), C(11), -0.09, -0.12 Å (E.s.d's on torsion angles and C displacements *ca.* 1° and 0.01 Å).

Although, because of the asymmetric side chain distribution, the host molecule, as a whole, has no symmetry, within a given molecule all twist boats have similar conformations and the same chiral sense. This imparts an approximate C_2 symmetry to the entire anthracene core, the non-crystallographic two-fold rotation axis runs through its centre and is roughly

perpendicular to its mean plane. This approximate C_2 symmetry also, to some extent, encompasses the location of the sulphur atoms.

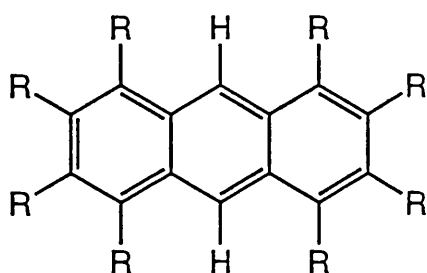
The cyclohexyl (128) and cycloheptyl (129) derivatives were also synthesised and were again purple crystals. They, however, have shown no inclusion ability, probably because the extra flexibility in the legs allows them to adopt a conformation where the molecule, as a whole, can close-pack without the need for a guest.

The camphorthio derivative (130) was also synthesised but could not be crystallised and only formed a purple glass. This could again be due to the flexibility of the leg, in this case rotation round the C_6-C_{10} and $C_{10}-S$ bonds, instilling a large amount of disorder into the molecule.

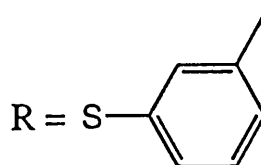


Rigidity appears to play an important role here, so it was decided to try to synthesise a few aromatic derivatives. The phenyl and *m*-tolyl derivatives were sought as potential hosts; however, even in the absence of light and at -10°C only a small amount of purple product was observed (by TLC) and could not be isolated. An orange product was isolated from the *m*-tolyl reaction and ^1H NMR suggests it to be 1,2,3,4,5,6,7,8-octakis(*m*-tolylthio)anthracene (131) obtained by leg cleavage of the fully substituted

anthracene. This suggests that the leg cleavage is much faster than with the alkyl derivatives, probably due to the aromatic ring's stabilising the sulphur radical, and so the fully substituted product is not stable under these conditions.

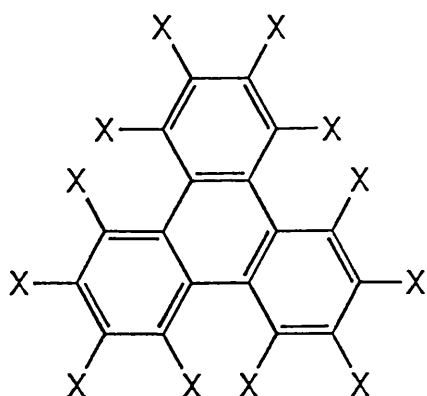


(131)



5.2.2 Triphenylene

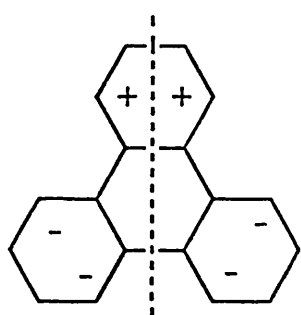
The next phase of the research involved investigation of the triphenylene core unit. There has been recent interest in the synthesis and structure of persubstituted triphenylenes^{220,221}, with a view to the stability of these strained molecules. It was not until recently, for example, that perchlorotriphenylene was synthesised and its structure elucidated by X-ray crystallography²²².



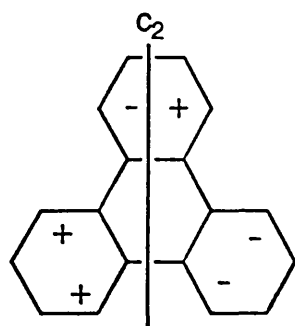
(122) : X = H

(132) : X = F

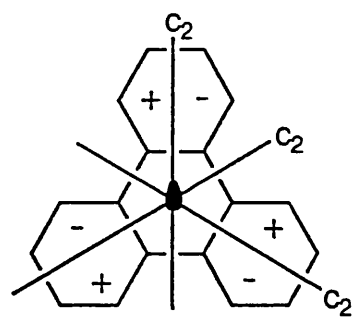
(133) : X = Cl



I



II
 C_2



III
 D_3

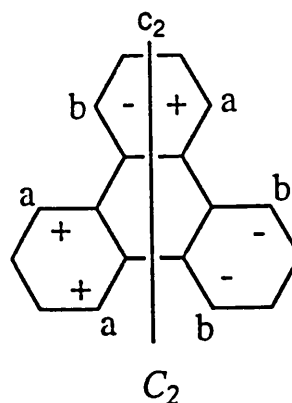
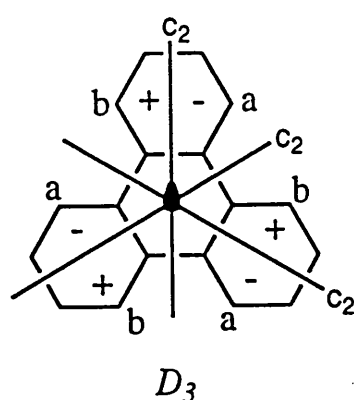
----- mirror pane

— C_2 rotation axis

● C_3 rotation axis

Triphenylene (122), itself, in the crystalline state adopts a conformation similar to that shown schematically in (I). The slight deviation from planarity is probably due to the steric effects of the *ortho*-hydrogens. As we increase the size of the substituents from H (1.2Å) to F (1.35Å) then a different conformation (C_2) is adopted (II) and the deviation from the plane is increased. It has also been suggested²²³ that (132) adopts a D_3 conformation (III) in solution, from ¹⁹F NMR work. The triphenylene (133) also adopts the C_2 conformation in the crystalline state, and it has been shown that although the D_3 form also corresponds to a true potential energy minimum²²², it is slightly higher in energy than the C_2 molecule.

As both C_2 and C_3 are prevalent in host systems then either of these conformations should aid clathrate formation. This leads to two possible conformations of the *ortho* substituents, assuming *anti* arrangement due to *peri*-interactions, namely *ababab* (D_3) or *abbaab* (C_2).

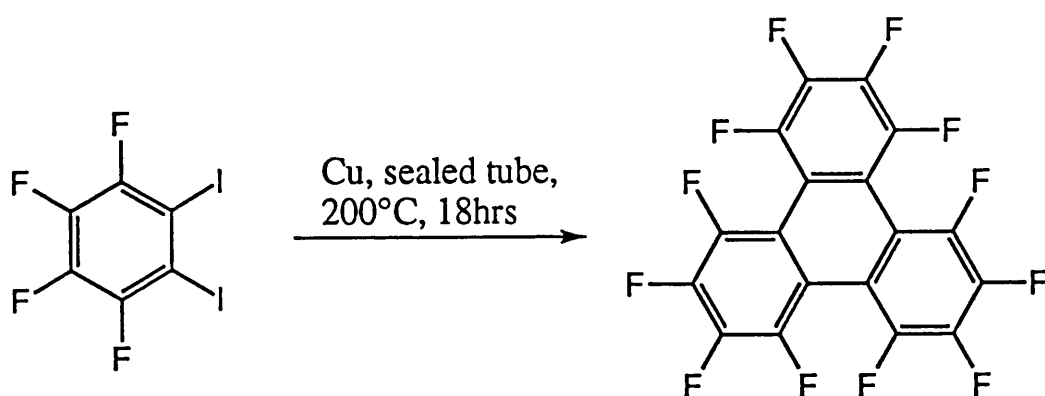


— C_2 rotation axis
 ● C_3 rotation axis

a, b- above, below the triphenylene core unit

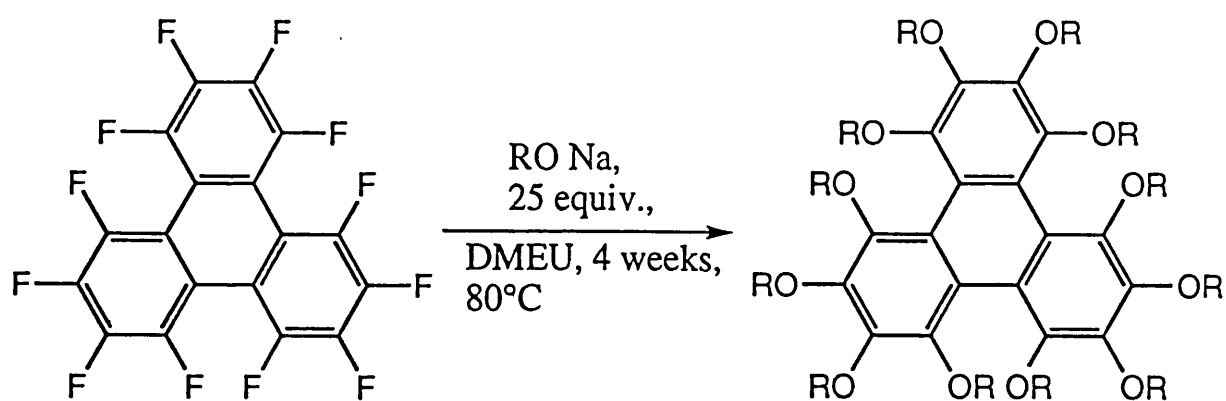
It was reasoned that although the persubstituted target molecules, like perfluorotriphenylene (132) and perchlorotriphenylene (133) would be strained they would, nevertheless be stable, and amenable to synthesis. It was, therefore, proposed to synthesise persubstituted triphenylenes with aromatic arms linked by a heteroatom.

The proposed starting material for the synthesis of the molecules was perfluorotriphenylene (132). This was prepared by utilising an Ullmann-type aromatic coupling reaction. 1,2-Diiodotetrafluorobenzene was reacted (Scheme 15) with copper bronze in a sealed tube at 200°C for 18 hours²²³. After extraction with dichloromethane a yellow oil was obtained which gave 4 - 5 spots on TLC. Separation by sublimation was attempted but no perfluorotriphenylene could be isolated so the mixture was then gravity columned on silica using pet. ether (40-60°C) as an eluent. In this way (132) could be isolated in about 25% yield. The compounds corresponding to the remaining spots on TLC, the dimer, tetramer and higher oligomers, were not isolated.

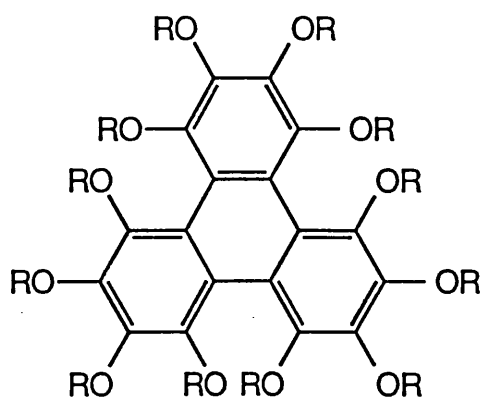


Scheme 15

First of all , oxygen was examined as the link heteroatom. These molecules were synthesised by reacting (132) with the appropriate phenolate anion, in DMEU, at 80°C for 4 weeks (Scheme 16). The molecules synthesised are shown in Table 3.



Scheme 16



OR	OR	OR
<p>(134)</p>	<p>(137)</p>	<p>(140)</p>
<p>(135)</p>	<p>(138)</p>	<p>(141)</p>
<p>(136)</p>	<p>(139)</p>	

Table 3. Structural formulae of persubstituted oxygen-linked triphenylenes
(134)-(141).

Dodecakis(phenoxy)triphenylene (134) was the first of this new class of molecule synthesised and it is indeed a stable colourless crystalline solid; however, it showed no propensity to include any solvent tried, crystallising unsolvated from chloroform/methanol, 1,4-dioxane/methanol and diethyl ether/hexane.

Next investigated was a variety of tolyl derivatives. *o*-Methylphenolate was reacted with perfluorotriphenylene, as before; unfortunately the resulting pale yellow oil consisted of a number of spots suggesting this anion did not react cleanly with (132) probably due to steric hindrance.

Dodecakis(*m*-methylphenoxy)triphenylene (135) was then synthesised. It was a pale yellow powder and was contaminated with another product (two spots on reverse phase TLC) which could not be separated from the fully substituted material.

The *p*-methylphenoxy derivative, dodecakis(*p*-methylphenoxy)triphenylene (136), was then synthesised and examined. Like the phenoxy derivative (134) it was a colourless crystalline solid that showed no clathration ability. (136) forms unsolvated crystals from dichloromethane/pet. ether (40-60°C), diethyl ether/pet. ether (40-60°C) and from 1,4-dioxane, 1,4-thioxane, *N*-methylmorpholine or acetonitrile with methanol. Single-crystal X-ray analysis of (136) revealed that it is orthorhombic (space group *Pbcn*). Like the perchloro- and perfluoro-

derivatives ((133) and (132) respectively) (136) adopts the C_2 conformation and, infact, the C_2 symmetry is not confined to the core unit as the entire molecule, located on a crystallographic two-fold proper rotation axis, possesses exact C_2 symmetry, with a conformation aababbaababb (Fig. 79).

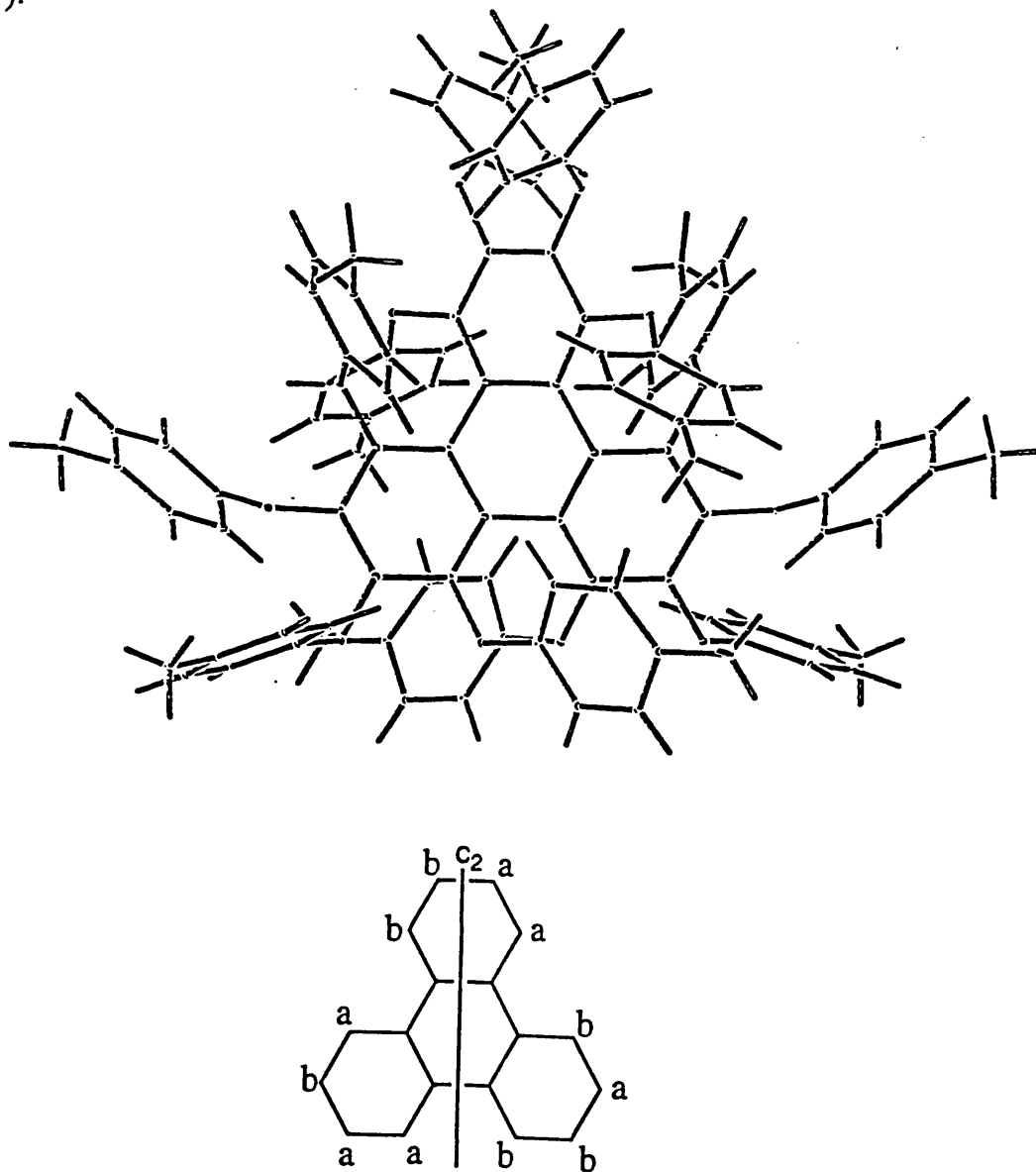


Fig. 79 Conformation of dodecakis(*p*-methylphenoxy)triphenylene (136).

The structure of the central core triphenylene unit of (133) and (136) are very similar and only differ in the size of the torsion angles and deviations from planarity. The torsion angle in (136), for the end-to-end twist is 45.2° (the two components which contribute to this are the central ring and ring C(7,5,6,6*,5*,7*), 29.0° and 16.2° respectively). This twist can be seen in Fig. 80. This is not as large as the end-to-end twist in (133) which is 56.6° (made up as before by 36.7° and 19.9°), which is probably due to the larger size of the chlorine atom over the oxygen atom. The other two rings, as in (133) adopt boat conformations. Fig. 81 shows the stereoview of (136) in its molecular crystal.

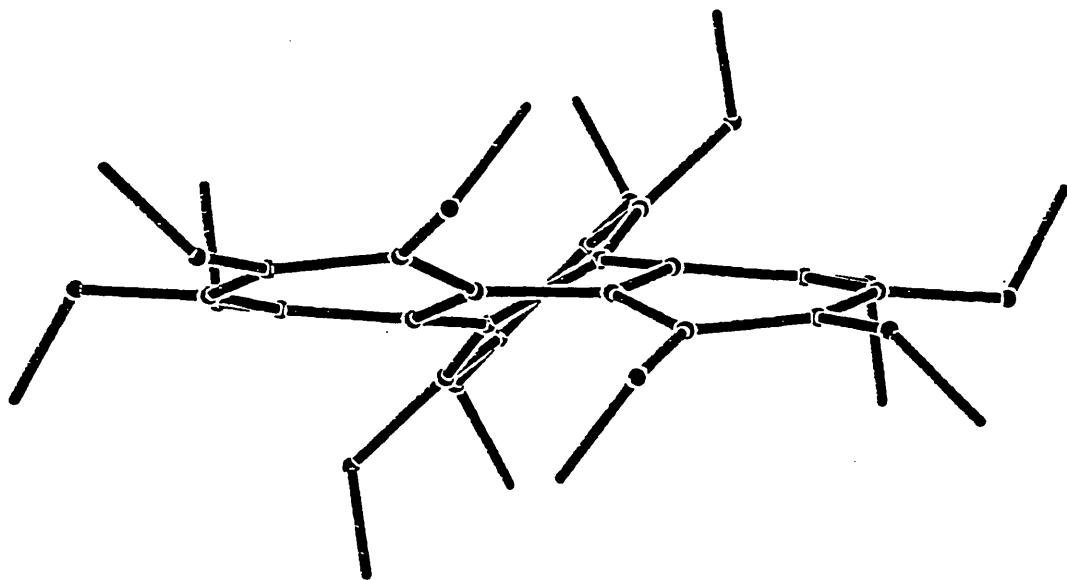


Fig. 80 Conformation of the central triphenylene core of (136) and attached oxygen atoms.

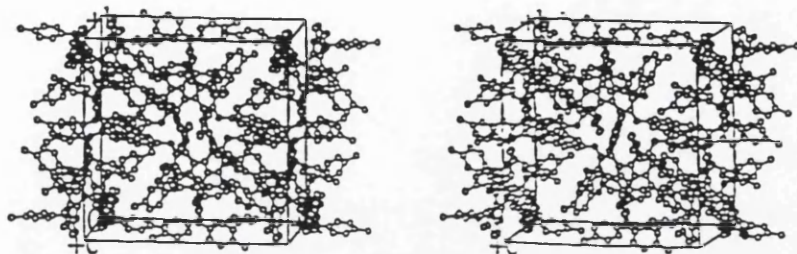
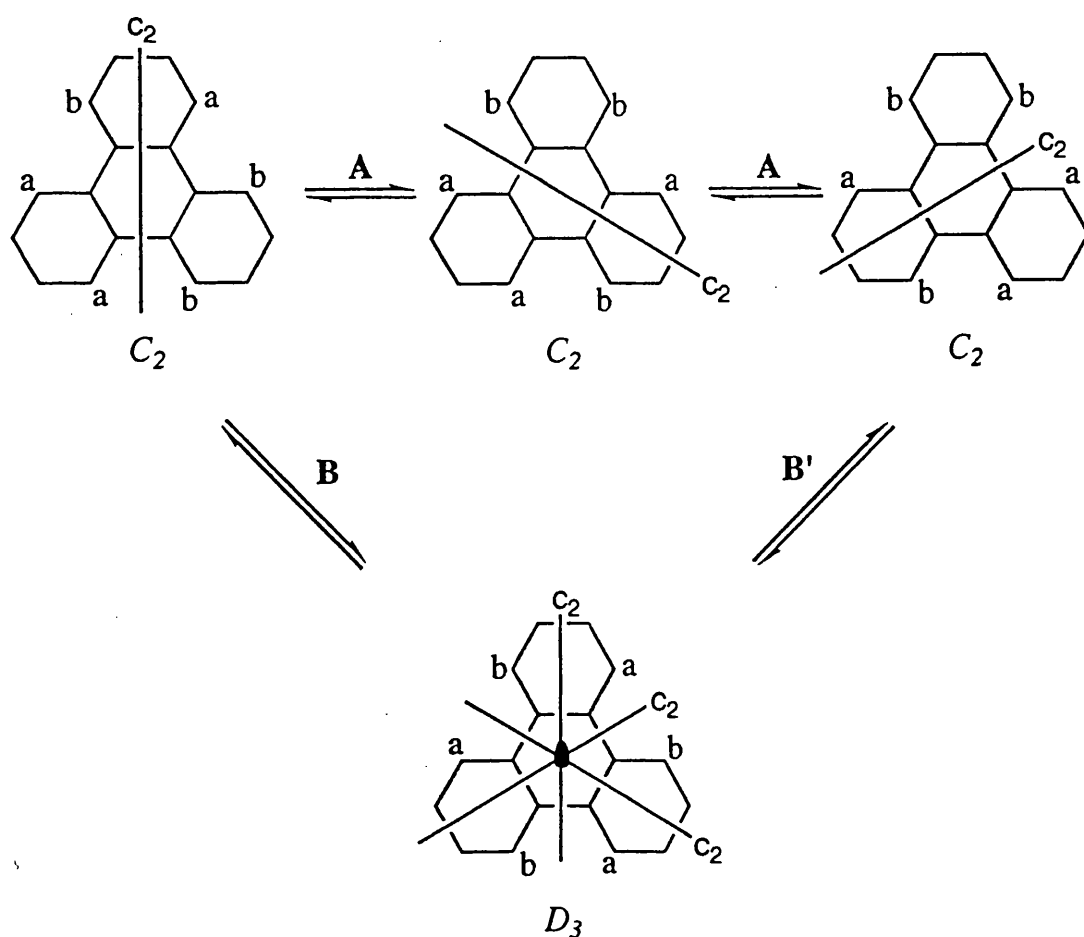


Fig. 81 Stereoview of dodecakis(*p*-methylphenoxy)triphenylene (136).

By ^1H NMR, only two CH_3 -Ar signals are observed. If the molecule has "frozen" C_2 symmetry then we would expect to see six such signals, assuming the absence of chance isochrony. This suggests that there is rapid interconversion of C_2 conformations. Whilst a (predominant) mixture of enantiomeric D_3 conformations would also explain the two CH_3 -proton resonances, this conformational situation is unlikely since these conformations are, in general for persubstituted triphenylenes, of higher calculated energy²²² than the C_2 counterparts. The most probable explanation corresponds to a predominance of enantiomeric C_2 conformations. Collapse of the six "frozen" CH_3 resonances can then occur by two distinct routes (Scheme 17) both routes leading to the observed two-line situation. In the route denoted A site exchange occurs with

enantiomerisation; in route B, B', which occurs via a D_3 conformation, collapse to a two-line CH_3 spectrum occurs without C_2 enantiomer interconversion. In principle, discrimination between these routes is possible if the racemisation rate (measured, for example, by low-temperature HPLC methods) can be compared with the rate of site-exchange measured by DNMR methods. However, when the ^1H NMR spectrum is measured at -100°C , although broadening of the two CH_3 resonance's is observed, no splitting occurs suggesting that facile interconversion still takes place even at low temperature.



Scheme 17

Targeting a more symmetrical arrangement of *meta* substituents, dodecakis(3,5-dimethylphenoxy)triphenylene (137) was synthesised but, like the *m*-methyl derivative (135), it was also an off-white powder that contained impurities which could not be separated from the fully substituted triphenylene (137).

The lack of success with the *ortho* and *meta* substituents led attention to be focused on different *para*-substituted derivatives, in the hope that alteration of the size of the *para*-substituent would disrupt the crystal lattice to such an extent that inclusion of a guest species would be essential to achieve close-packing.

With this in mind, the synthesis of a number of *para*-substituted derivatives was undertaken, and dodecakis(*p*-*t*-butylphenoxy)triphenylene (138) was synthesised. Although this was a highly crystalline solid, again no inclusion ability was found. At this point it was decided to synthesise derivatives with much larger *para*-substituents, hence, both dodecakis(*p*-cumylphenoxy)triphenylene (139) and dodecakis(*p*-naphthylphenoxy)triphenylene (140) were prepared. These, however, were both off-white powders, that did not exhibit inclusion properties. This could possibly be due to the *para*-substituent's being too large and consequently completely disrupting the crystal lattice. This led to the idea of introducing an intermediate-sized *para*-substituent and so dodecakis(*p*-phenylphenoxy)triphenylene (141) was synthesised. This did indeed form

clathrates with molecules such as acetonitrile, 1,4-dioxane and glymes (see Table 4).

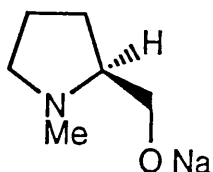
On exposure to air these crystals cloud rapidly, suggesting ready guest loss. The speed at which the crystals cloud seems to be related to the boiling point of the guest, for example, the acetonitrile (b.p. 82°C) clathrate clouds in a matter of seconds whereas the diglyme (b.p. 162°C) clathrate clouds after about 30 minutes. The guests included and the ease of loss of such guests suggest that (141) forms a channel complex.

Guest	Host : Guest (Ratio)	Method of Analysis ^(a)
acetonitrile	2 : 1	¹ H NMR
1,4-dioxane	1 : 1	¹ H NMR
diglyme	1 : 1	¹ H NMR
triglyme	ca. 1 : 1	¹ H NMR
tetraglyme	2 : 1	¹ H NMR

(a) ¹H NMR at 200 MHz.

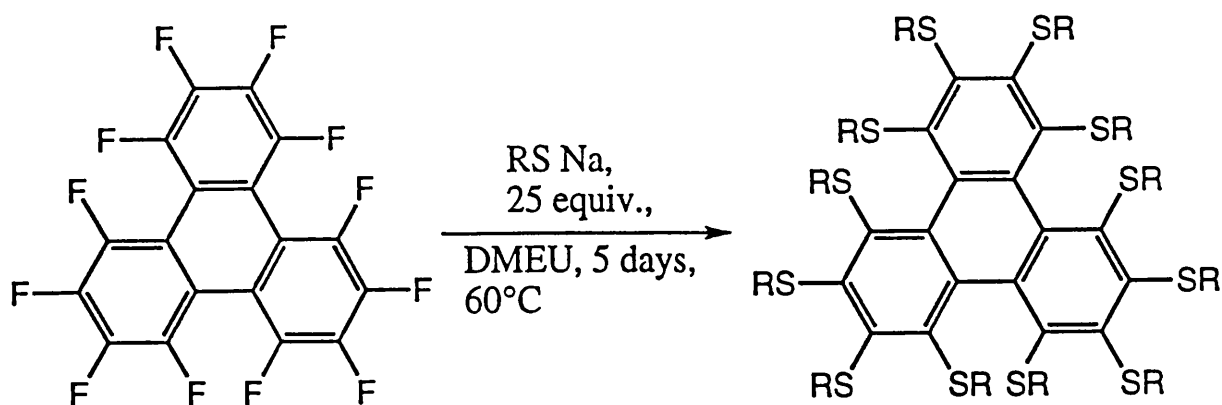
Table 4. Inclusion compounds formed by dodecakis(*p*-phenylphenoxy)triphenylene (141).

In an attempt to make a chiral derivative of the oxygen-link triphenylene type, for potential use as enantiomer separation, perfluorotriphenylene was reacted with sodium (*S*)-(-)-1-methyl-2-pyrrolidinemethoxide, however no pure product could be isolated.

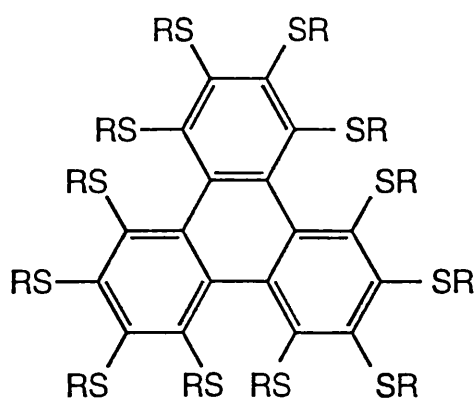


The study was then broadened to encompass sulphur-linked triphenylenes in order to determine whether increasing the size of the hetero-atom (which was expected to increase the twist of the triphenylene core) would promote or, indeed, hinder inclusion ability.

These molecules were synthesised employing a route paralleling that used for the oxygen-linked counterpart, though, since a sulphur-based anion is a better nucleophile than an oxygen-based one towards carbon centres of interest here, a reaction time of only 5 days, at 60°C was required (Scheme 18).



Scheme 18

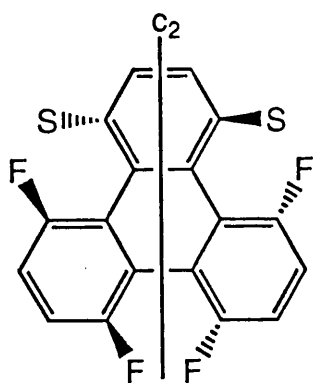


SR	SR	SR
 (142)	 (144)	 (146)
4 x F; 8 x (143)	 (145)	

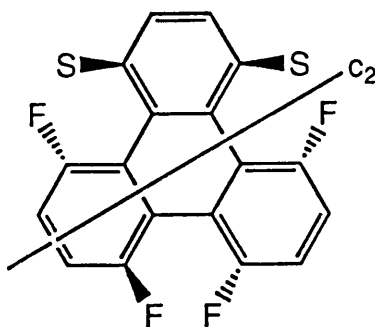
Table 5. Structural formulae of sulphur-linked triphenylenes (142)-(146).

The first sulphur-linked analogue examined was dodecakis(phenylthio)triphenylene (142). Unlike the oxygen derivative (134), which is a highly crystalline colourless solid, (142) was a powdery material (red-brown in colour) showing that no direct comparison between

the two series can automatically be assumed. If the reaction is terminated after 3-4 hours, when reacted at room temperature, then an intermediate is isolated as red-brown crystals. Mass spectra showed this to be the octa-substituted triphenylene unit (143), and the ^{19}F NMR spectrum shows only two fluorine signals of equal intensity. This suggest that the molecule possesses a symmetrical structure. Assuming that all the fluorines left are *ortho* fluorines this gives two possible structures I and II, in which, unspecified substituents correspond to sulphur.



IV (+ enantiomer)



IV' (non-exact rotational axis
(see text))

Both these peaks are triplets with a splitting of *ca.* 7 Hz. This is consistent with the view that II is the correct structure for octakis(phenylthio)tetrafluorotriphenylene (143). Interestingly, the ^{19}F NMR spectrum shows significant broadening of the triplet at -89 ppm at low temperature (-80°C), indicating that the fluorine atoms undergo site exchange. This observation reveals that (143) does not exist exclusively as an enantiomeric mixture of C_2 conformations (IV) since this situation would

not involve site-exchange: the observed site-exchange implies that other conformations exist, for example, IV' in which the triphenylene skeleton has only *approximate* C_2 symmetry.

Dodecakis(*p*-methylphenylthio)triphenylene **(144)** was synthesised, purified by gravity column chromatography and recrystallised from diethyl ether to give orange crystals. The ^1H NMR spectrum shows six, equal-intensity methyl peaks suggesting that this molecule is C_2 -symmetric and, unlike the oxygen series, there is no conformational interconversion significant on the NMR time-scale corresponding to either route A or route B, B' in Scheme 17. The existence of substantial amounts of the D_3 conformation (which would have to be in slow exchange with the C_2 form, to avoid collapse of the methyl resonances) is precluded since no additional methyl resonances are present. This change in flexibility is attributable to the size of the sulphur atoms, their increased bulk hindering facile conformational interconversion. In order to establish whether the C_2 -conformation found in solution is also found in the solid state, a single-crystal X-ray structure analysis of **(144)** was carried out. The crystals are triclinic (space group $P\bar{1}$) and the molecule was found to adopt a **bbabbabbabaa** conformation A (Fig. 82).

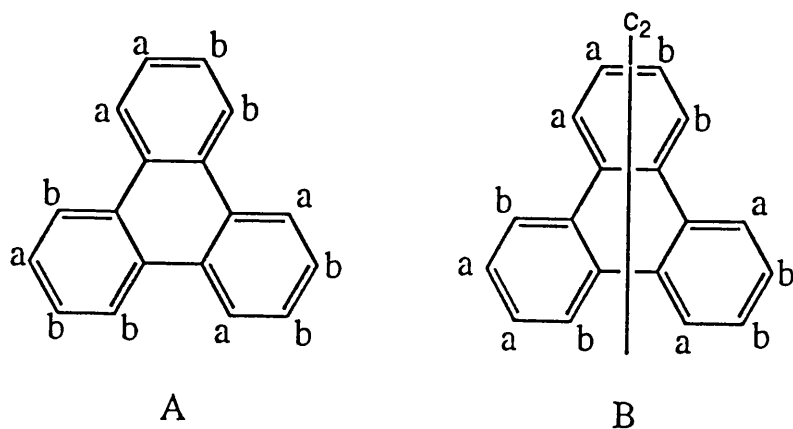


Fig.82 A comparison of (A) the orientations of SAr side-chains of (144) with respect to the mean plane of the triphenylene core, and (B) the locations of the sulphur atoms with respect to the same mean plane. In each case a and b denote, respectively, above and below this mean plane.

Occupying a general position, molecule (144) possesses no exact crystallographic symmetry, contrasting with the exact C_2 symmetry of the *p*-methylphenoxy counterpart (136) in its molecular crystal. As can be seen from Fig. 82 (A), an overall asymmetry is imparted to (144) by orientation mismatch of two SAr side-chains. However, the central part of the molecule, comprising the aromatic core and attached sulphur atoms closely approximates to C_2 symmetry.

The torsion angle in **(144)** for the end-to-end twist is 51.7° (the two components which contribute to this are the central ring and the ring C(1) - C(6), 30.6° and 21.1° , respectively). This is about 6° larger than the end-to-end twist observed in the oxygen-linked analogue **(136)** and this is consistent with the ^1H NMR results. The extent of the twist can be appreciated from Fig. 83.

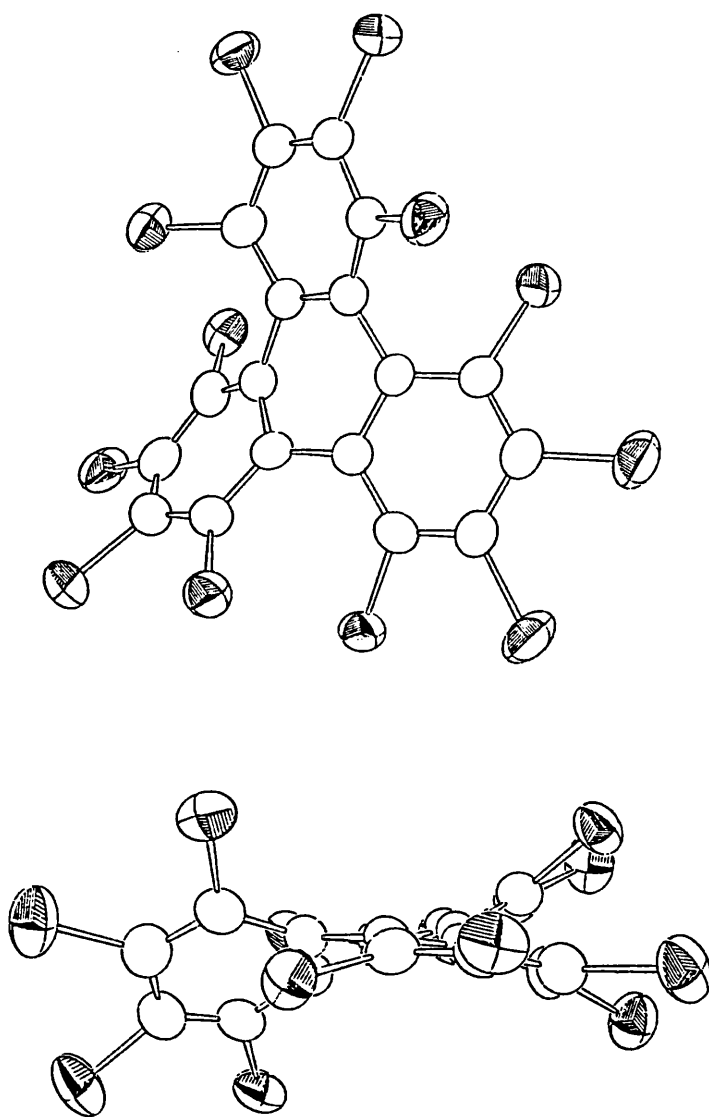


Fig. 83

Two views of the **(144)** triphenylene core unit.

The benzene rings of the triphenylene unit have boat conformations. Fig. 84 shows a stereoview of one molecule of (144); whilst Fig. 85 shows a stereoview illustrating the molecular packing of (144) in its triclinic crystal.

^1H DNMR studies of (144) at 200 MHz in d^8 -toluene as solvent reveal an equal broadening of all six methyl proton resonances at elevated temperatures; at 90°C , in the lifetime broadening region, a free energy of activation, ΔG , of *ca.* 20 kcal.mol^{-1} , can be estimated for the interconversion of C_2 conformations. At the present, however, it is not possible to say whether the interconversion occurs by route A or route B, B' (or by both) in Scheme 17.

Dodecakis(*p-t*-butylphenylthio)triphenylene (145) was prepared and purified by gravity column chromatography to give orange unsolvated crystals from diethyl ether/pet. ether ($40\text{-}60^\circ\text{C}$). The ^1H NMR spectrum at 200 MHz shows, at ambient temperatures, six equal-intensity singlet resonances corresponding to the six different *t*-butyl groups of a C_2 -symmetric conformation analogous to that of (144). However in this case, unlike (144), when the solution is heated to 100°C no significant line broadening occurs. This indicates that, in contrast to the *p*-methyl analogue (144), there is no interconversion of the C_2 conformers on the NMR time-scale at 100°C . This reduced conformational flexibility for (145) almost

certainly reflects the extra bulk of the *t*-butyl group which leads to increased difficulty in reorienting the SAr side-chains.

Dodecakis(3,5-dimethylphenylthio)triphenylene (146) was then synthesised, purified by gravity column chromatography and recrystallisation from diethyl ether/pet. ether (40-60°C) to give orange crystals that, so far, have shown no propensity to include any guest species, crystallisation from 1,4-dioxane/methanol, chloroform/methanol and diethyl ether/pet. ether (40-60°C) giving unsolvated crystals.

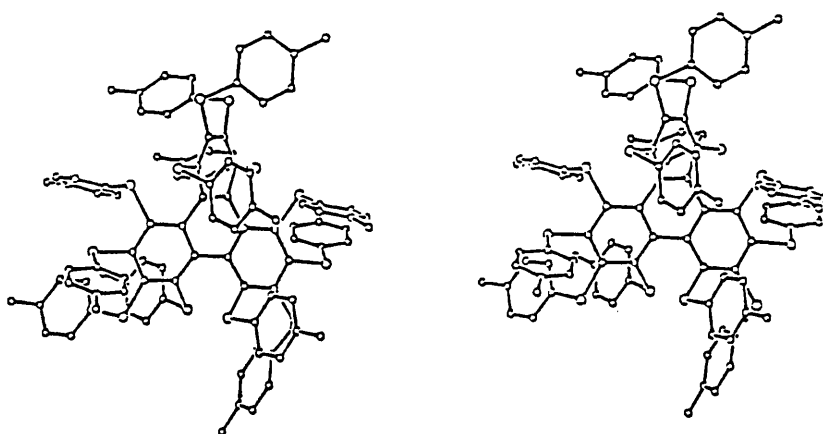


Fig. 84 A stereoview of one molecule of (144) showing its conformational arrangement.

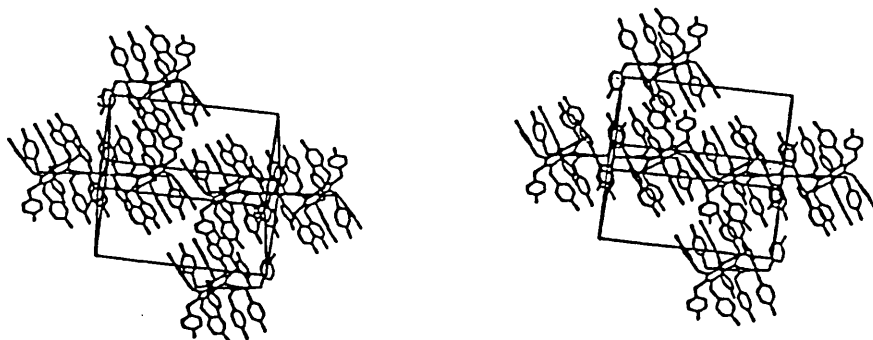


Fig. 85 A stereoview illustrating the molecular packing of (144) in its triclinic crystal.

Persubstituted alkylthio triphenylenes were also sought, unfortunately however, both the cyclohexylthio and cyclopentylthio derivatives gave mixtures of products. No isolation of either of these products was obtainable by chromatography and so no further analysis was carried out on these potentially interesting systems.

5.3. Linking the Hexa-hosts

Having expanded the study of fused aromatic cores (see Section 5.2), it was decided to initiate a new line of investigation. Could one design novel clathrates by linking two hexa-hosts together? (Fig. 86).

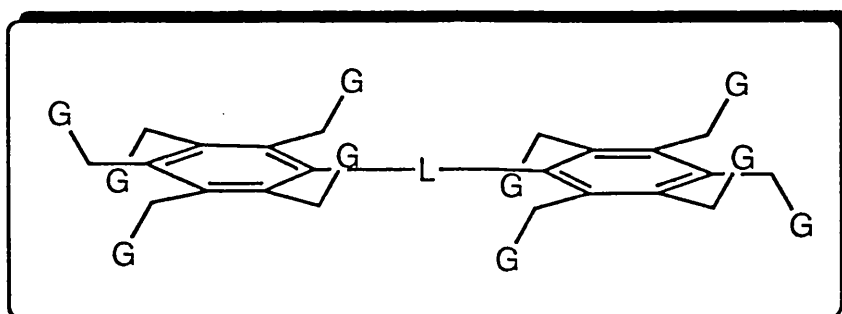
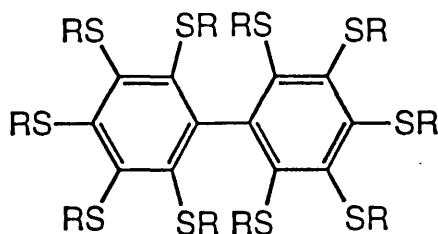
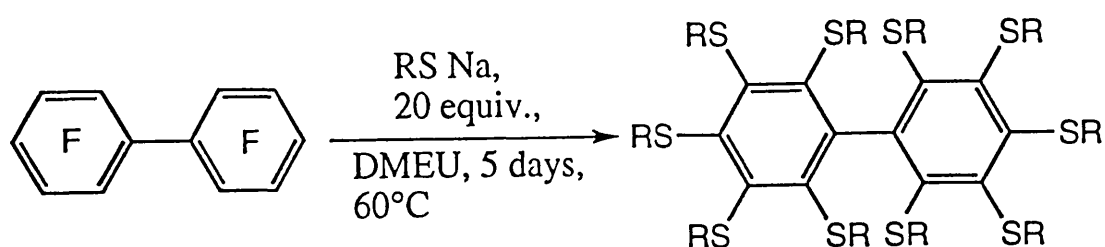


Fig. 86 Schematic representation of a linked hexa-host, in which L represents a linking unit joining two persubstituted aromatic rings. The unit L may be a single atom, a chain of atoms, or even a single covalent bond.

These next Sections will describe the results obtained from this study.

5.3.1. Biphenyl-based systems

This is the first in the series of linked pentasubstituted benzene units to be described. Here L is just a covalent bond. In order to study the possibility of obtaining host compounds based on biphenyl, the decathioethers (147)-(150), the structure of which are shown in Table 6, were selected as targets.



SR	SR
 <u>(147)</u>	 <u>(149)</u>
 <u>(148)</u>	 <u>(150)</u>

Table 6 Structural formulae of decathioethers (147)-(150) related to biphenyl.

These were all synthesised from perfluorobiphenyl under similar conditions used for the persubstituted triphenylene compounds i.e. with the appropriate sodium arenethiolate or cycloalkanethiolate, in DMEU, for 5 days, at 60° C.

Decakis(phenylthio)biphenyl (147) and decakis(cyclohexylthio)biphenyl (149) are non-crystalline solids, however both decakis(*p*-

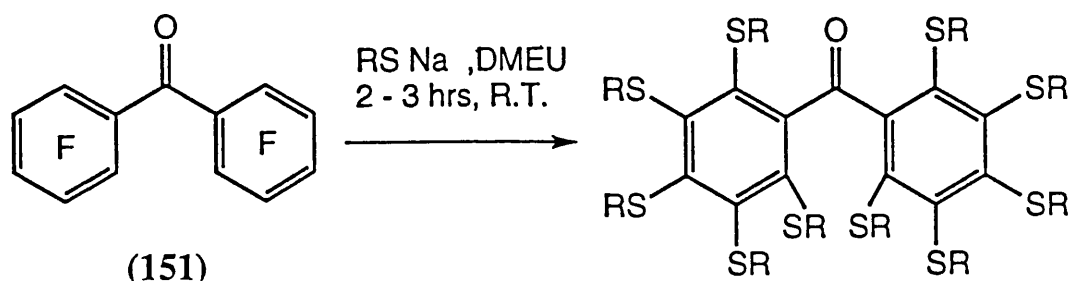
methylphenylthio)biphenyl (148) and decakis(cyclopentylthio)biphenyl (150) form yellow crystals. Compounds (148) and (150) did not show any propensity to include guest molecules, crystallising unsolvated from a variety of solvents such diethyl ether, hexane, chloroform, 1,4-dioxane and methanol.

The fact that in both the biphenyl and the triphenylene series the phenylthio derivatives, (147) and (142), are non-crystalline and the *p*-methylphenylthio derivatives, (148) and (144), are crystalline, but not hosts, suggests that there might be some correlation. It is possible that as for the oxygen triphenylene series, what is required for these cores is extended side-chain units in order to prevent close packing of the molecules and so promote clathrate formation, a suitable side-chain worthy of consideration in this context being the *p*-phenylphenylthio group.

5.3.2 Benzophenone-based Systems

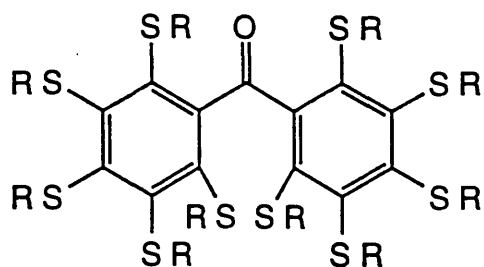
Further studies extended this idea of linking two penta-substituted benzene rings from a covalent bond to a one-atom link. The first one-atom link system examined was based on benzophenone, where the link unit is C(O), this being facilitated by the commercial availability of the starting material, decafluorobenzophenone (151). The prospective host molecules

were synthesised by reacting (151) with appropriate thiolate anions in DMEU, at room temperature, for 2-3 hours (Scheme 19).



Scheme 19

Table 7 shows the fifteen benzophenone based decathioethers that were prepared in the present study.



SR	SR	SR
 (152)	 (157)	 (162)
 (153)	 (158)	 (163)
 (154)	 (159)	 (164)
 (155)	 (160)	 (165)
 (156)	 (161)	 (166)

Table 7. The molecular structures of benzophenone based decathioethers
(152)-(166).

Decakis(phenylthio)benzophenone (152) was the first of these synthesised. It was purified by gravity column chromatography and recrystallised from a 1,4-dioxane/methanol mixture to give the 1,4-dioxane clathrate, host-guest ratio 2 : 3. Compound (152) was then recrystallised from a variety of solvents and the results are shown in table 8. Because of the low solubility of (152) in many solvents, chloroform was often used as a co-solvent. This gave some interesting information on selective clathration behaviour, for example, chloroform is favoured over, albeit that their concentrations differed, oxalic acid, whereas 1,4-dioxane, DMF, ethane-1,2-dithiol and DMEU are included to a greater extent than chloroform. Both acetic acid and glycol form clathrates of (152) with chloroform also incorporated into the crystal lattice, i.e. ternary complexes are formed.

Solvent Mixture	Guest(s)	Host-Guest Ratio	Method of Analysis ^(a)
1,4-dioxane/CHCl ₃ /methanol	1,4-dioxane	2 : 3	¹ H NMR, MA, TGA
oxalic acid/ CHCl ₃ /methanol	CHCl ₃	1 : 1	MA, TGA
DMF/CHCl ₃ /methanol	DMF	1 : 1	¹ H NMR, TGA
DMEU/CHCl ₃	DMEU	ca. 1 : 1	¹ H NMR
<i>N</i> -methyl morpholine ^(b)	<i>N</i> -methyl morpholine	1 : 2.6	¹ H NMR
CHCl ₃ /acetic acid	CHCl ₃ , acetic acid	1 : 1 : 1	¹ H NMR, TGA
CHCl ₃ /acetic acid (after drying)	CHCl ₃	1 : 1	¹ H NMR, MA
glycol/CHCl ₃ /methanol	CHCl ₃ , glycol	2 : 2 : 1	¹ H NMR
ethane-1,2-dithiol/ CHCl ₃ /methanol	ethane-1,2-dithiol	4 : 3	¹ H NMR

(a) ¹H NMR at 200 MHz; MA - Microanalysis; TGA - Thermal Gravimetric Analysis.

(b) Dissolved by heating in a sealed tube.

Table 8. Crystalline inclusion compounds formed by decakis(phenylthio)benzophenone (152).

Thermogravimetric analysis (TGA) suggests that host (152) forms a fairly tight clathrate with chloroform as this complex is stable upto 135°C. The chloroform (b.p. 61°C) is lost between 135°-160°C. The 1,4-dioxane clathrate loses its guest in two stages 105°-160°C and 170°-190°C. This possibility suggests that the 1,4-dioxane guest component is in two different cavity types. This could explain why the ternary clathrates are formed with chloroform in one cavity and, for example, acetic acid in the other. This view is consistent with the fact that when crystals of the $\text{CHCl}_3 \cdot \text{CH}_3\text{COOH} \cdot \text{(152)}$ are heated, at 80°C, under vacuum for 4 hrs, the acetic acid is removed but the chloroform remains in the host lattice. Host (152) also includes ethane-1,2-dithiol to form yellow odourless crystals that are stable up to 170°C. This confers on this host the potential to be used as a molecular storage or "crystal" bottle (See Section 4.2) for containment of this odorous guest, which is a synthetically useful reagent.

In order to elucidate the architecture of this host-guest system single-crystal X-ray work was initially carried out on the chloroform/acetic acid inclusion compound. These crystals are monoclinic (space group $P2_1/c$). Fig. 87 shows the structure of (152) in the molecular crystal. It possesses an **ababababab** conformation, **a** being the side-chain oriented above the plane of the benzene ring in the same direction as the C=O bond. Fig. 88 shows a stereoview of the molecular packing of the clathrate. The chloroform guest

molecules are ordered and can be seen running down the centre of the unit cell. The acetic acid could not be located probably due to its being disordered in the second type of void.

To examine the effect of substitution of a methyl group in the side-chain, the general synthetic route described for (152) was employed to prepare decakis(*p*-methylphenylthio)benzophenone (153) and decakis(*m*-methylphenylthio)benzophenone (154). Both molecules were found to be new hosts, including 1,4-dioxane on recrystallisation from this solvent, the respective host-guest ratios being 1 : 1.8 and 1 : 1. Host (154) also includes acetonitrile, host-guest ratio 1 : 1.

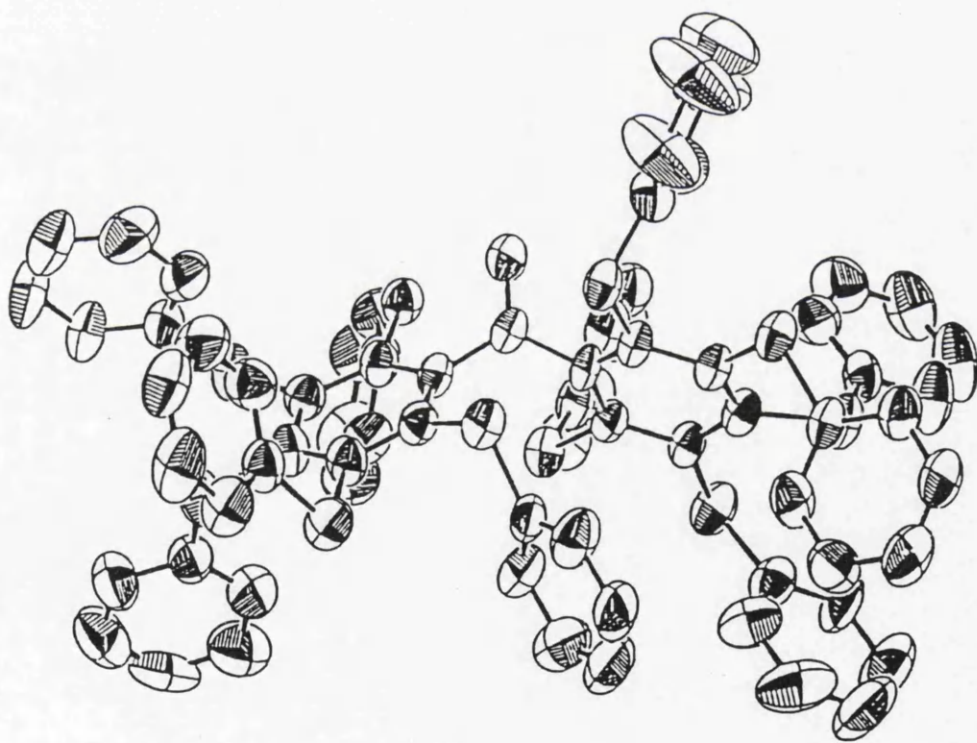


Fig. 87 An illustration of the structure and conformation of (152) in its (1 : 1 : 1) inclusion compound with chloroform and acetic acid.

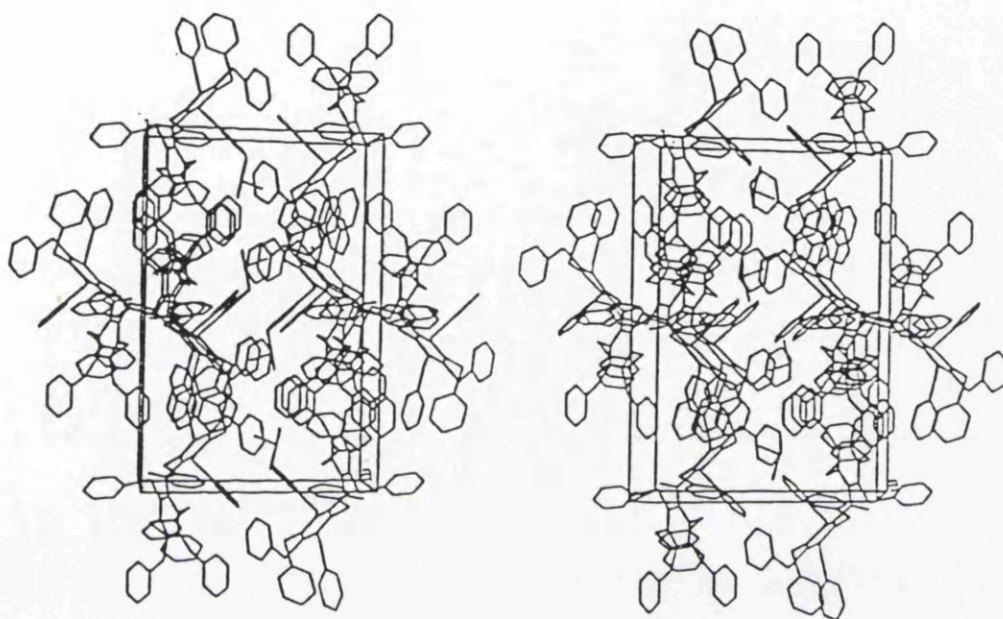


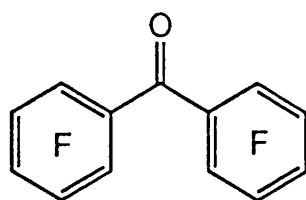
Fig. 88 A stereoview showing the molecular packing in the (1 : 1 : 1) inclusion compound of (152) with CHCl_3 and CH_3COOH . The (highly disordered) acetic acid guest component has not been located and is not shown.

The effect of introduction of two methyl groups was also studied and compounds decakis(3,5-dimethylphenylthio)benzophenone (155) and decakis(3,4-dimethylphenylthio)benzophenone (156) were prepared.

Although (155) gave an inclusion compound (host-guest ratio 4 : 1) with 1,4-dioxane, on recrystallisation from a 1,4-dioxane/diethyl ether/methanol mixture, and a DMF adduct, host-guest ratio 5 : 2, its isomer (156) was only obtained as an unsolvated yellow powder. This indicates a critical dependence on the substitution pattern of the methyl groups.

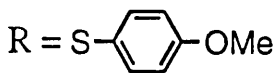
The more highly substituted molecule decakis(3,4,5-trimethylphenylthio)benzophenone (157) purified by recrystallisation from diethyl ether/pet. ether (40-60°C), was obtained in the form of unsolvated yellow crystals. Compound (157) has shown no ability to include any guest, recrystallising unsolvated from 1,4-dioxane, acetonitrile, chloroform and methanol mixtures, for example. Also decakis(*p-t*-butylphenylthio)benzophenone (158), in which the side-chain bears a bulky *para*-substituent, exhibits no capacity for inclusion compound formation.

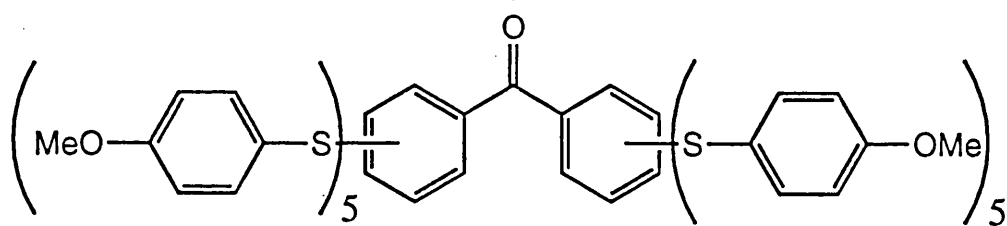
Introduction of a *para*-hydroxy group was achieved as shown in Scheme 20, compound (160) being prepared in a two-step process via decakis(*p*-methoxyphenylthio)benzophenone (159) which is subsequently demethylated by BBr₃. The introduction of the polar *para*-substituents in (159) and (160) completely eliminates host properties and these compounds were only obtained as yellow powders.



(151)

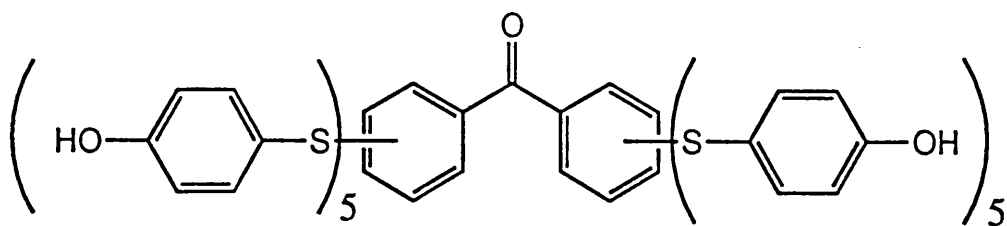
RS Na, DMEU
1 - 2 hrs, R.T.

R = S--OMe



(159)

BBr₃



(160)

Scheme 20

Paralleling the formation of a powdery material found for the 3,4-dimethyl case (156), decakis(5-indano)benzophenone (161), which has a trimethylene chain linking the 3- and 4-carbon atoms of the side-chain's aromatic ring, was obtained only as a yellow foam. These results are an expression of the difficulty these molecules have in forming a stable crystal lattice. Interestingly, though, an additional methyl group in the 5 position, as in (157), does allow ready crystal formation. Difficulty in attaining a suitable crystal packing may also be inferred for decakis(β -naphthylthio)benzophenone (162) which was also obtained only as a yellow foam; it may be noted that this side chain corresponds to fusion of a benzene ring onto the 3 and 4 positions of the ring directly attached to sulphur.

All the compounds in the benzophenone series described so far were aryl derivatives, now cases where the sulphur atom is attached to an aliphatic carbon are considered. The first of these decakis(cyclopentylthio)benzophenone (163) was prepared analogously to the previous compounds, purified chromatographically and recrystallised from a mixture of diethyl ether and methanol. Compound (163) was found to possess versatile host properties. Table 9 indicates guests which form crystalline inclusion compounds with host (163).

Guest	Host : Guest Ratio	Method of Analysis ^(a)
1,4-dioxane	1 : 1	¹ H NMR, MA, TGA
DMF	3 : 1	¹ H NMR
acetonitrile	1 : 1	¹ H NMR
chloroform	3 : 1	¹ H NMR

(a) ¹H NMR at 200 MHz; MA - Microanalysis; TGA - Thermal Gravimetric Analysis.

Table 9. Crystalline inclusion compounds formed by host decakis(cyclopentylthio)benzophenone (163).

TGA suggests that the (1 : 1) clathrate of (163) is reasonably stable since the 1,4-dioxane is lost at 125-145°C. In order to elucidate this adduct's structure single-crystal X-ray work was attempted, however, at room temperature a satisfactory data set could not be obtained; this was attributed to pronounced thermal motion of the cyclopentyl rings. At lower temperature, surprisingly, the crystal did not diffract; and this could be due to the cyclopentyl legs' being frozen out in different positions and so making the molecules disordered (disorientated) in the crystal.

Decakis(cyclohexylthio)benzophenone (164) was obtained as yellow crystals which upon recrystallisation from chloroform/DMF gave yellow

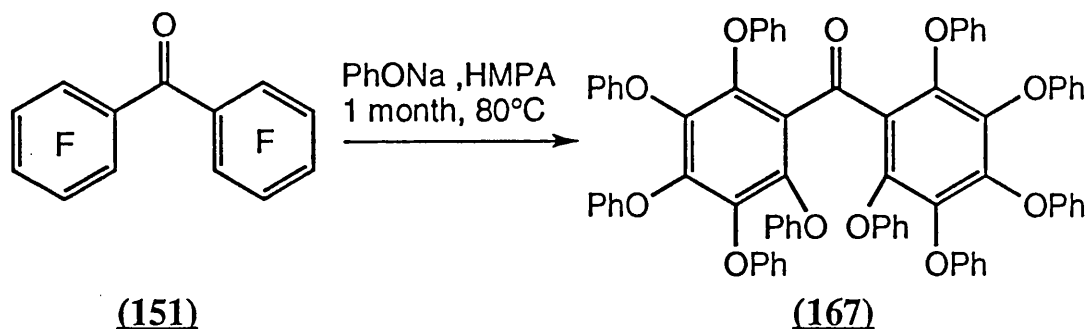
needles of the DMF inclusion compound, host-guest ratio *ca.* 2 : 1 (by ^1H NMR). Due to lack of time this compound was, unfortunately, not further investigated.

The benzophenone based design idea has uncovered an excellent series of host molecules. This led to attempts to synthesise chiral examples of these host compounds. The first attempt involved a camphor-based side-chain as the chiral source and decakis(10-*S*-camphorthio)benzophenone (165) was purified by flash-column chromatography. Repeated attempts to recrystallise the resulting powder, however, failed, and so another chiral derivative was sought. Using (+)-1-phenylethylthiol, decakis((+)-1-phenylethylthio)benzophenone (166) was synthesised and purified chromatographically. Unfortunately, like the camphor derivative (165), it also was a yellow powder that showed no signs of crystallising.

In summary, although no chiral example has yet been found, suitable achiral decathioethers based on benzophenone do indeed exhibit significant inclusion properties, and this represents the first successful application of the idea that one can link two hexa-host units, here with a one-atom link, thereby producing new series of host molecules.

It was of interest to establish whether corresponding decaethers would also possess inclusion characteristics, so parent molecule decakis(phenoxy)benzophenone (167) was prepared by reacting

perfluorobenzophenone with sodium phenolate in HMPA, at 80°C, for 1 month (Scheme 21).



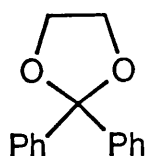
Scheme 21

After purification via gravity column chromatography and recrystallisation from diethyl ether/methanol, clear, colourless, unsolvated crystals of (167) were obtained. Decaether (167) was also recrystallised from 1,4-dioxane/methanol in order to investigate any inclusion ability, however, unlike its decathioether counterpart (152), (167) showed no signs of forming a clathrate. Due to lack of time no further inclusion experiments were carried out.

The single comparison of the PhS- and PhO- persubstituted benzophenones, (152) and (167) respectively, indicates a marked contrast in ability to form inclusion compounds; the former is a versatile inclusion host whilst the latter has given no indications of adduct formation to date. Whether members of the oxygen series with suitable side-chains will, in

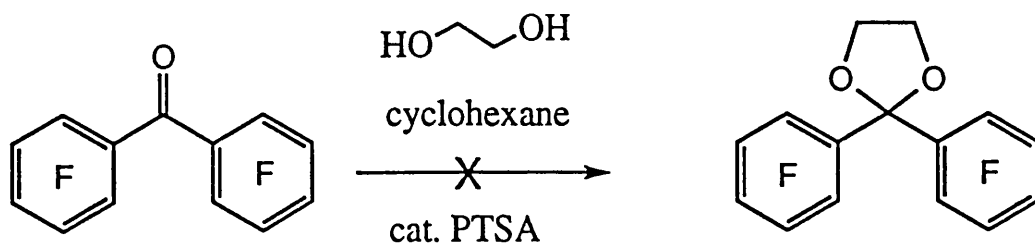
fact, possess host properties is not known at present. Further work to establish this would certainly be justified.

Following the positive results obtained for decathioethers related to benzophenone, described above, work was directed towards varying the unit linking the hexa-host units and the first modification attempted corresponds to replacing the benzophenone moiety with the diphenyldioxolane building block (168).



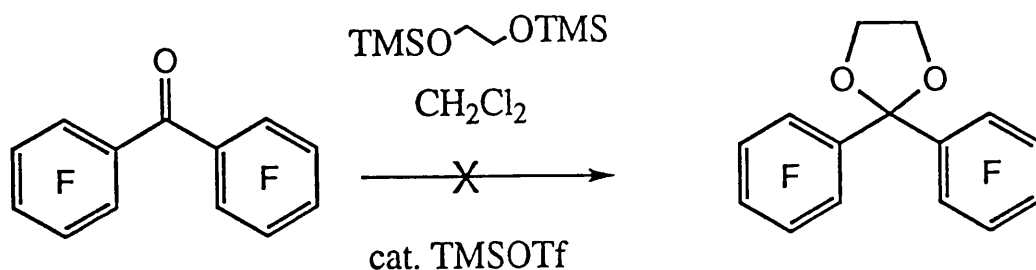
(168)

To this end, decafluorobenzophenone was reacted with ethylene glycol under acidic in a Dean-Stark apparatus (Scheme 22), however, no reaction was observed and starting material was recovered.



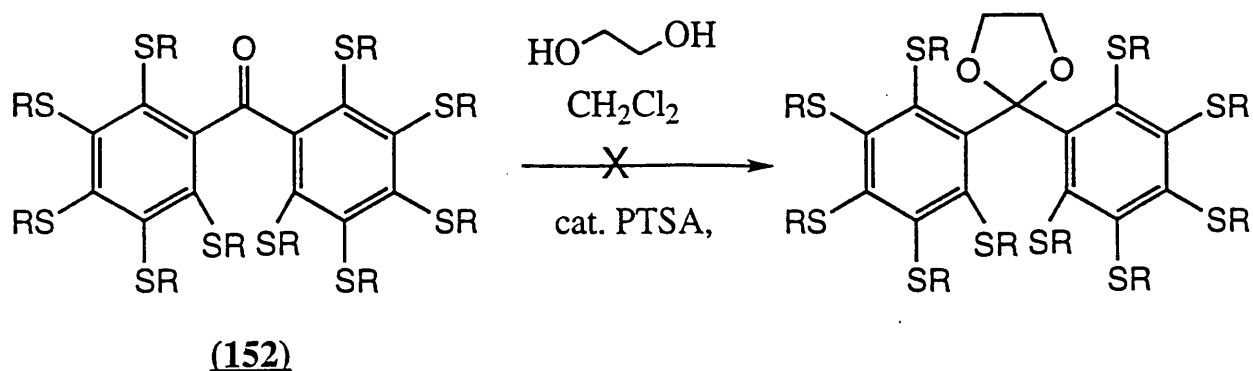
Scheme 22

Ketal formation under these conditions is reversible so with this in mind decafluorobenzophenone was reacted with bis(trimethylsiloxy)ethane in the presence of a catalytic amount of trimethylsilyltriflate²²⁴ (Scheme 23).



Scheme 23

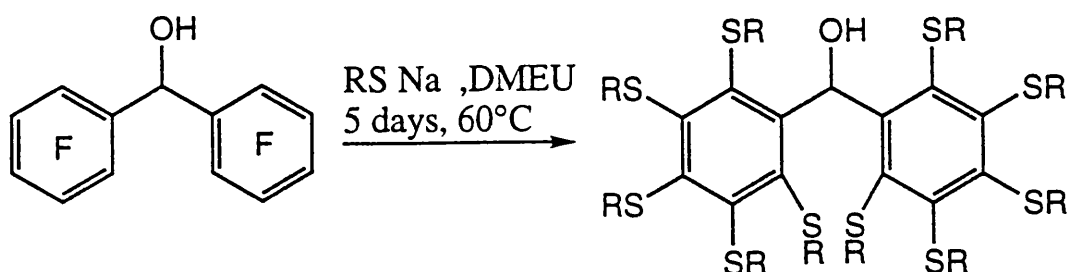
This method exploits formation of a ketal under aprotic conditions and is irreversible, so if any product is formed it should be not be converted back to starting materials; however, as before only starting materials were obtained. It is believed that the electron withdrawing properties of the C₆F₆ groups deactivates the carbonyl, thus preventing its reacting. An alternative synthetic route was also tried, namely direct reaction of a deca-substituted benzophenone with ethylene glycol. Decakis(phenylthio)benzophenone (**152**) was reacted with ethylene glycol in the presence of acid (Scheme 24). Both TLC and ¹H NMR indicate that no reaction occurred, this time probably due to steric hindrance of the carbonyl group by the SPh side-chains.



Scheme 24

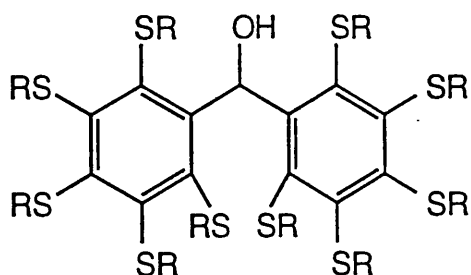
5.3.3 Benzohydrol-based Systems

In order to determine the role of the structure of the one-atom link, persubstituted benzohydrol derivatives were investigated, these systems having an altered oxidation state at the central carbon. The persubstituted benzohydrols were synthesised by reacting decafluorobenzohydrol with the appropriate sodium arene- or cycloalkane-thiolate in DMEU, at 60°C, for 5 days (Scheme 25).



Scheme 25

Table 10 shows the structures of the persubstituted benzohydrols, (169)-(171), prepared in this study.



SR	SR	SR
(169)	(170)	(171)

Table 10. Structures of the persubstituted benzohydrols, (169)-(171).

Decakis(phenylthio)benzohydrol (169) was synthesised, purified by gravity column chromatography, to give yellow crystals of the DMF inclusion compound (*ca.* 1 : 1).

Encouraged by the above result, it was decided to investigate the side-chain, the β -naphthylthio unit, which did not confer any inclusion ability in the benzophenone series. The appropriate benzohydrol (170), like its benzophenone counter part (162), could not be made to crystallise and was obtained only as a yellow foam.

Attempts were then made to synthesise persubstituted cycloalkylthiobenzohydrols. Decakis(cyclohexylthio)benzohydrol (171) was therefore prepared, purified chromatographically, and recrystallised from chloroform/DMF/methanol to give yellow needles. Although no proof of inclusion was obtained, there was not enough time to fully study compound (171). The synthesis of the cyclopentyl derivative was also attempted, however the reaction produced a complex mixture of products, none of which could be isolated and so no further analysis was carried out.

Overall, the limited information available from comparison of the benzophenone and benzohydrol series suggests that a parallel may exist between these two series. The compounds (152) and (169), both exploiting the PhS- side-chain are inclusion hosts, whilst compounds (162) and (170) with common side-chain β -naphthylS- do not crystallise and form only foams.

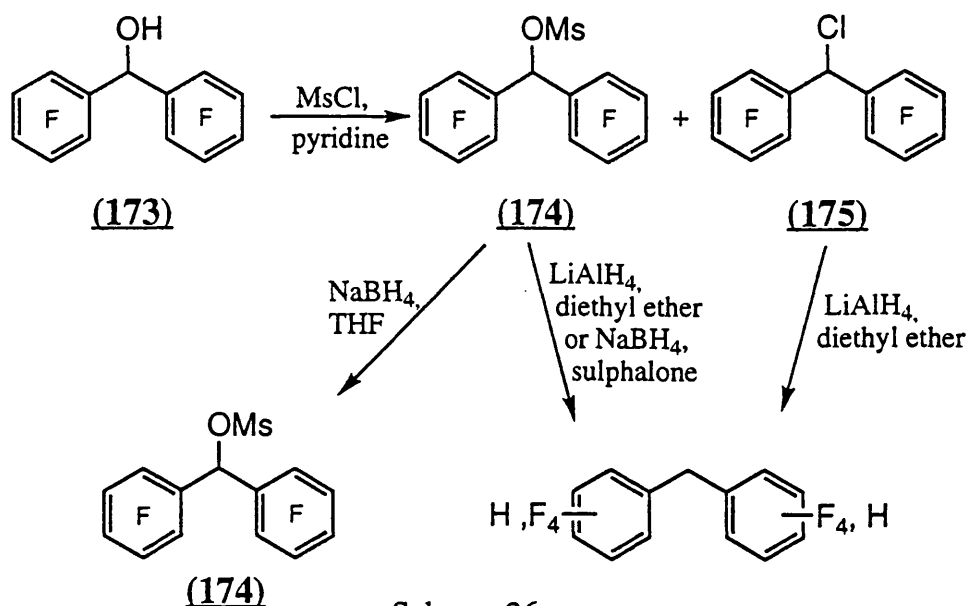
5.3.4 Diphenylmethane-based Systems

The next step was to look at the one-atom link with no oxygen attached to the central carbon atom, that is persubstituted diphenylmethane-based systems.

The proposed starting material decafluorodiphenylmethane (172), is not commercially available and so an attempt was made to synthesise it by

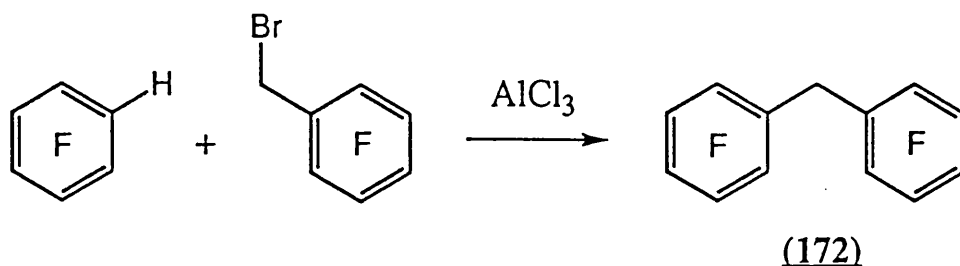
reductive removal of the OH group of decafluorobenzohydrol (**173**), the proposed route was to convert the hydroxy group into the mesylate group which could be subsequently removed by LiAlH_4 .

On reaction of decafluorobenzohydrol with mesyl chloride in pyridine a mixture of mesylated product (57%) (**174**) and bis(pentafluorophenyl)methane chloride (36%) (**175**) was obtained. This was separated easily by flash-chromatography. LiAlH_4 reduction of the mesylate (**174**) and the chloride (**175**) removed the MsO and Cl substituents but, unfortunately also replaced two of the ring fluorine atoms with hydrogen. NaBH_4 being a milder reducing agent was then tried, but no reaction was observed in THF. NaBH_4 in sulpholane has been reported to be a stronger reducing agent, so it was then reacted with the mesylate (**174**) but the same over reduced product was obtained as for the reaction with LiAlH_4 (Scheme 26).



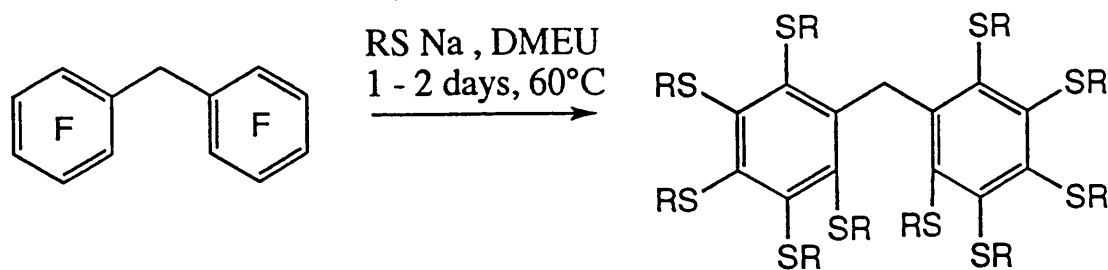
Scheme 26

After having encountered problems with the above route a different approach was sought and so a Friedel-Crafts reaction was tried²²⁵. Pentafluorobenzene was reacted with pentafluorobenzyl bromide in the presence of AlCl_3 . This gave (172) in around 35% yield (Scheme 28).

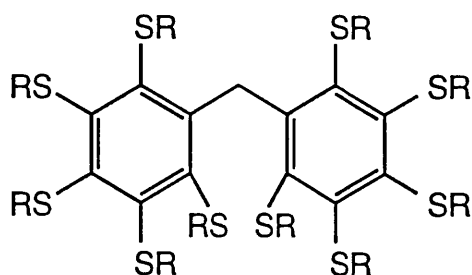


Scheme 27

Having obtained (172), it was then reacted with the appropriate sodium arene- or cycloalkane-thiolate in DMEU, at 60°C , for 2 days (Scheme 28).



Scheme 28



SR	SR
(176)	(177)

Table 11. Structures of the deca-substituted diphenylmethanes (176) and (177).

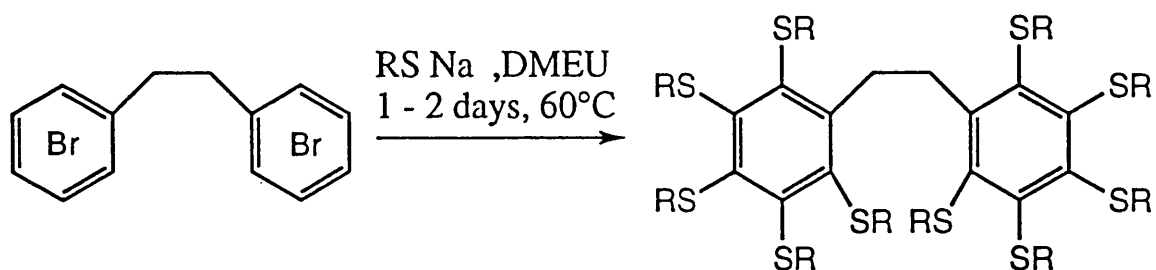
The compounds selected for study, bis[penta(phenylthio)phenyl]methane (176) and bis[penta(cyclopentylthio)phenyl]methane (177) were prepared as above, chromatographically purified, and each was recrystallised from a 1,4-dioxane/methanol mixture. This gave crystalline inclusion compounds containing 1,4-dioxane as the guest component, the respective host-guest ratios for (176) and (177) being 3 : 2 and 1 : 1. TGA of the 1,4-dioxane

adduct of (176) shows that the 1,4-dioxane is retained to 140°C, this guest (b.p. 101°C) being subsequently lost between 140 and 170°C.

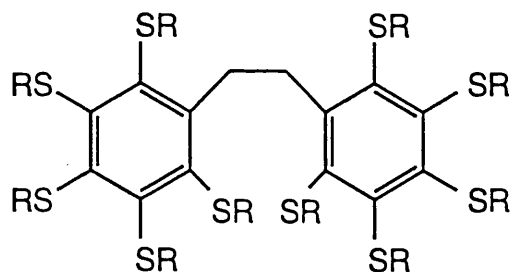
As with the benzohydrol series the diphenylmethane derivatives seem to parallel the benzophenone series in ability to form clathrates, although a more extensive study has to be done to prove this. It should be noted that although inclusion ability may be conferred by a given side-chain across these series, the host-guest ratios encountered for a given guest may vary from host to host. In addition, it is interesting to note that, uniformly across the benzophenone, benzohydrol and diphenylmethane series, molecules deca-substituted with the PhS- side-chain always possess inclusion ability.

5.3.5 The 1,2-diphenylethane framework: a two-atom link system

Having proved that the idea of linking hexa-hosts is a viable strategy for the design of novel hosts an attractive possibility was to extend the length of the link to the two-atom series, and persubstituted 1,2-diphenylethanes were investigated. Compounds of this type were prepared by reacting 1,2-bis(pentabromophenyl)ethane (178) with the appropriate sodium thiolate salt in DMEU, at 60°C, for 2 days (Scheme 29). Table 12 shows the five compounds, (179)-(183), that were synthesised.



Scheme 29



SR	SR
<p><u>(179)</u></p>	<p><u>(182)</u></p>
<p><u>(180)</u></p>	<p><u>(183)</u></p>
<p><u>(181)</u></p>	

Table 12. Structures of the deca-substituted 1,2-diphenylethane compounds

(179) - (183)

1,2-Bis[pentakis(phenylthio)phenyl]ethane (179) was purified by gravity column chromatography and recrystallised from 1,4-dioxane/methanol to give unsolvated yellow crystals. A single-crystal X-ray study was undertaken to elucidate the structure and conformation of (179) in its molecular crystal. The crystals are monoclinic, space group $P2_1/n$.

The molecule of (179) is illustrated in Figs. 89 and 90. It is located on a point of $\bar{1}$ symmetry and is therefore, constrained to be centro-symmetric. In an extension of the earlier nomenclature the molecule possesses an *ababa(a,l)(b,l)babab* conformation, the new symbols *a,l* and *b,l* referring to the orientation of the first non-directly attached link atom or group, here CH_2 , above or below the mean plane of the molecule.

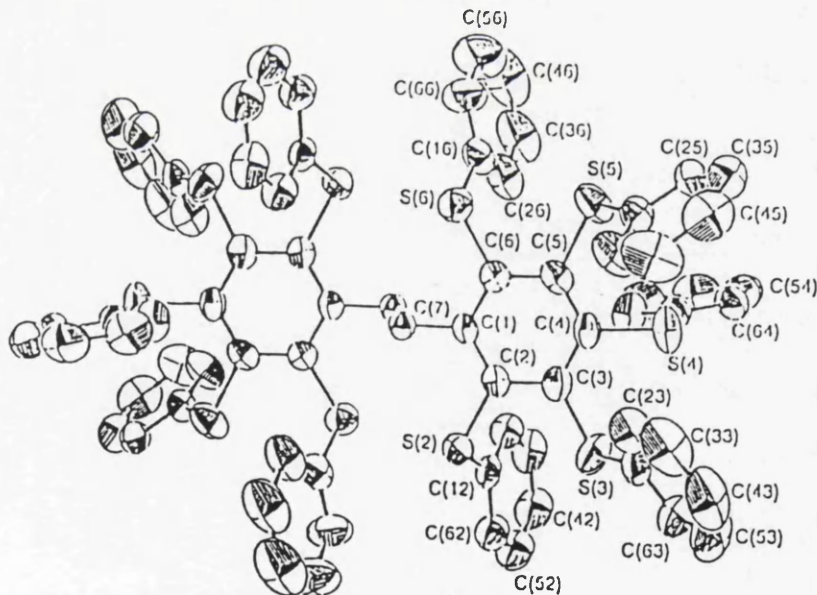


Fig.89 The structure of bis[pentakis(phenylthio)phenyl]ethane (179) in its molecular crystal.

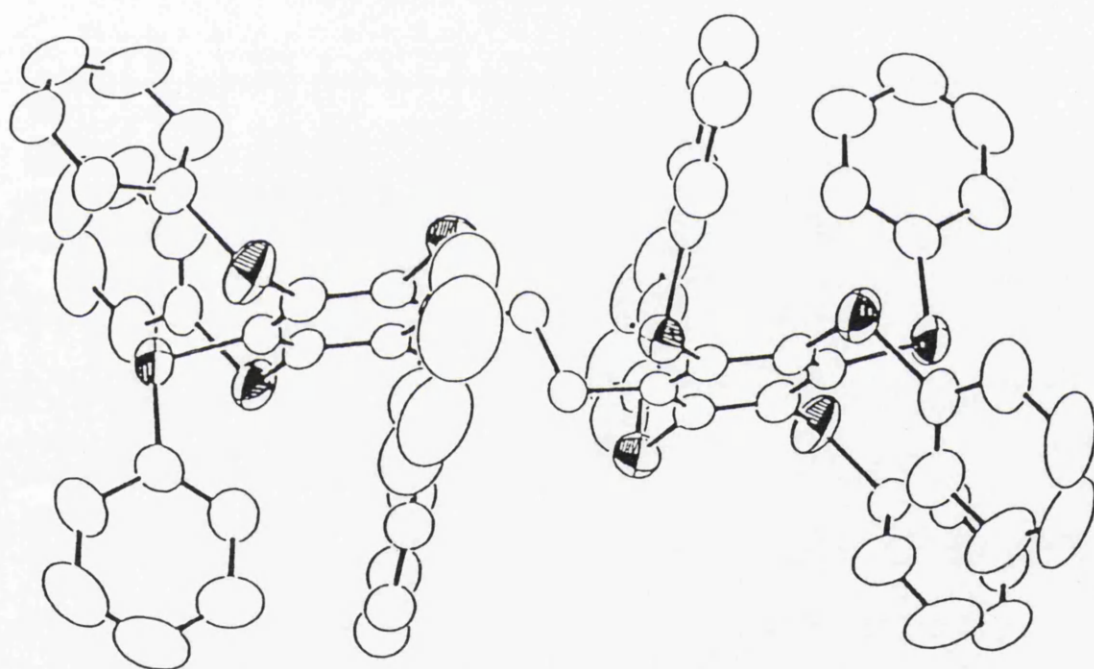


Fig. 90 A view illustrating the conformation of (179) in its molecular crystal.

As may be best appreciated from the stereoview in Fig. 91, the PhS side-chain units exhibit the maximum possible degree of alternation above and below the mean plane of the central 14 carbon atoms. The disposition of the five crystallographically independent PhS units is described by the representative torsion angles -62° and 33° for C(core)-C(core)-S-C(leg).

These torsion angles may be compared with the corresponding values of 56° and 28° found for the unique PhS side-chain in the trigonal CCl_4 clathrate of hexakis(phenylthio)benzene. Bond lengths and angles are in keeping with expected values.

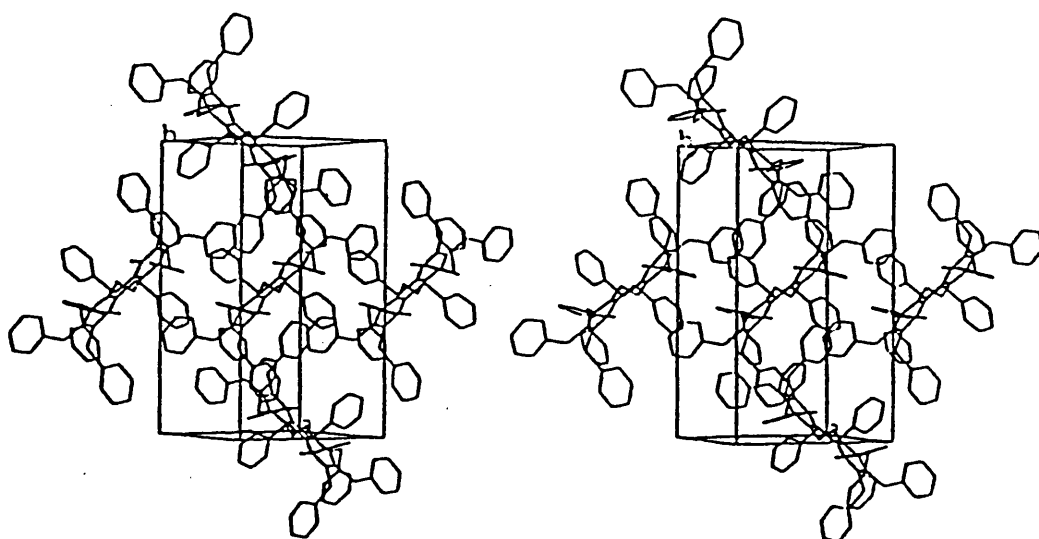


Fig. 91 A stereoview illustrating the molecular packing in the unsolvated crystal of (179).

The carbon atoms C(1) - C(6) of the benzene core unit deviate significantly from planarity, and with exception of S(5) which lies close to the mean benzene plane, the sulphur atoms also show significant displacements from the mean benzene plane.

(179) was also recrystallised from diethyl ether/pet. ether (40-60°C) and chloroform/methanol. In each case unsolvated crystals of (179) were obtained.

1,2-Bis[pentakis(*p*-methylphenylthio)phenyl]ethane (180) and 1,2-bis[pentakis(*p*-*t*-butylphenylthio)phenyl]ethane (181) were examined to see what effect, if any, *para*-substitution of the side-chain had on potential inclusion characteristics.

Compounds (180) and (181), prepared and purified analogously to (179), both gave unsolvated yellow crystals from diethyl ether/pet. ether (40-60°C) mixtures. Compound (180) also gave unsolvated crystals from 1,4-dioxane/methanol. To investigate the effect of *meta*-substitution of the side-chain's aromatic ring 1,2-bis[pentakis(3,5-dimethylphenylthio)phenyl]ethane (182) was similarly prepared and purified. Recrystallisation of (182) from diethyl ether/pet. ether (40-60°C) gave unsolvated yellow crystals, and further recrystallisation experiments have given no indication of inclusion compound formation by (182).

Finally in this series, cycloalkylthio-substituted compounds were briefly investigated. 1,2-Bis[pentakis(cyclohexylthio)phenyl]ethane (183) was obtained as an off-white solid which exhibited no propensity to form inclusion compounds, crystallising unsolvated from diethyl ether/pet. ether (40-60°C) and chloroform/methanol. Synthesis of the corresponding cyclopentylthio compound was also attempted, however, the resulting oil contained a number of products, none of which could be isolated.

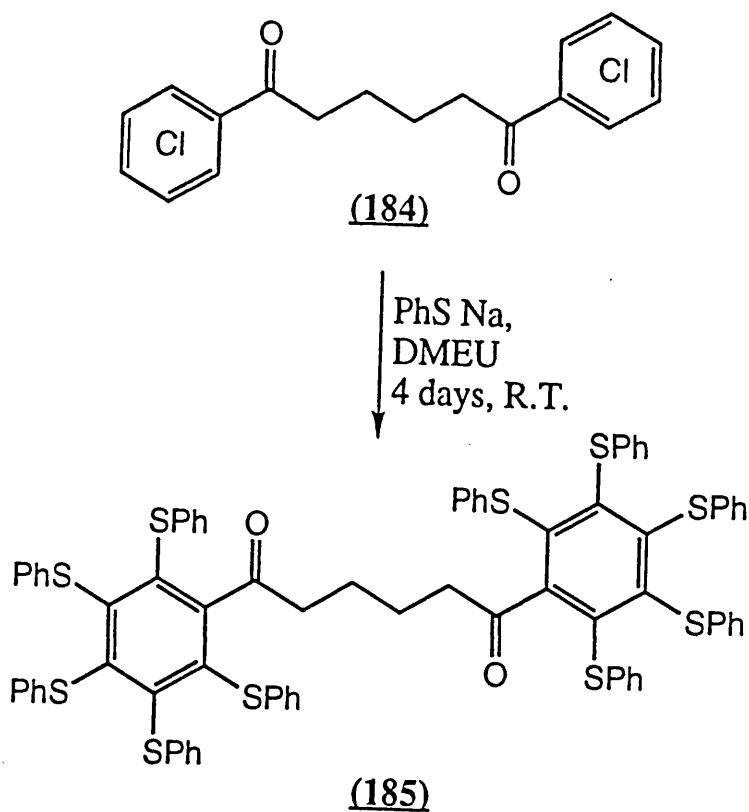
In summary, one observes a complete removal of any ability to form inclusion compounds when an extra carbon atom is introduced into the link joining the two penta-substituted benzene rings. This is probably due to an increase in flexibility in the link which allows the molecule to adopt a conformation that does not need to include a guest in order to close-pack. This close-packing may well be facilitated by location of the molecule at a centre of inversion, as for (179), a situation impossible (without disorder) for the V-shaped single-atom link counterparts.

5.3.6. 1,6-Diphenylhexa-1,6-dione-based Systems

The rigidity of the central link seems to be an important factor controlling whether or not a given central framework will be compatible with inclusion compound formation. In order to further test this idea,

pentasubstituted benzenes attached by a relatively long chain (six carbon atoms) was synthesised.

1,6-Bis[pentakis(phenylthio)]hexa-1,6-dione (**185**) was prepared by treatment of 1,6-bis(pentachlorophenyl)hexa-1,6-dione (**184**) with sodium benzenethiolate in DMEU, at room temperature, for four days (Scheme 30).



Scheme 30

Compound (185) was purified by gravity column chromatography and recrystallisation from diethyl ether/pet. ether (40-60°C). In keeping with the view that increased conformational mobility of the central chain decreases the likelihood of inclusion compound formation, (185) was found to show no evidence of guest incorporation, this compound crystallising unsolvated from diethyl ether/pet. ether (40-60°C) and chloroform/methanol.

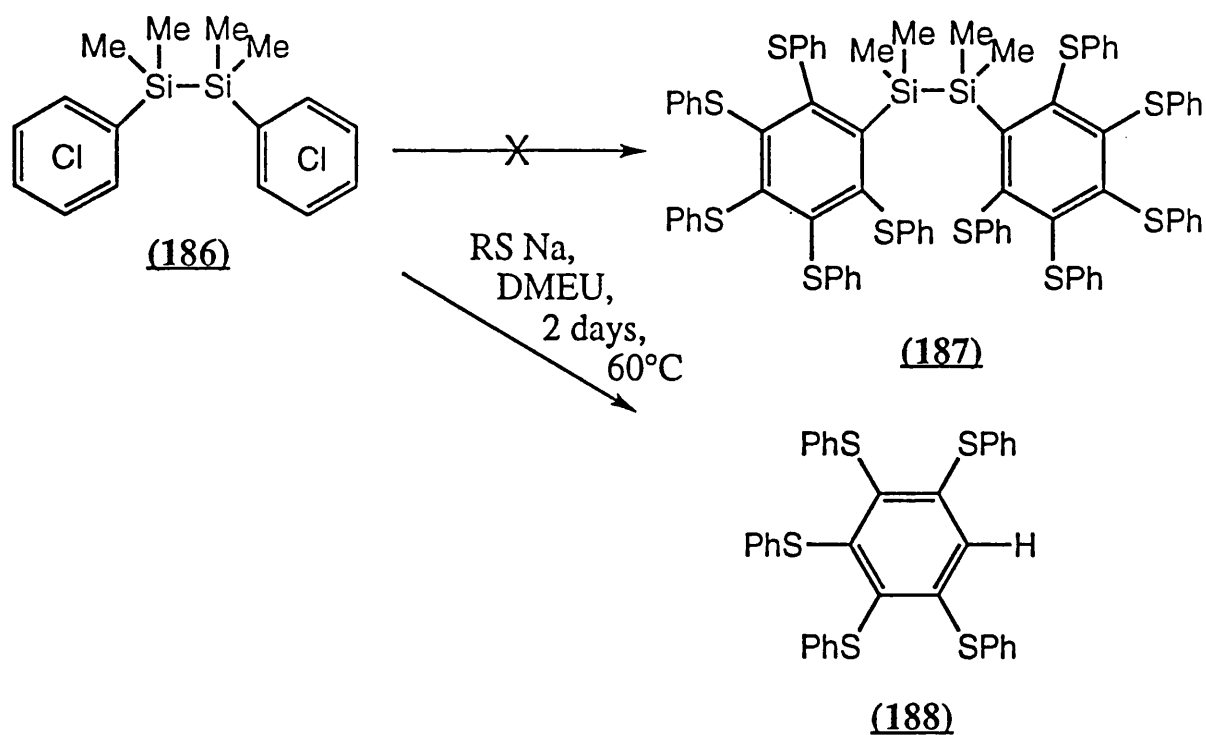
It is interesting to note that compound (185) may achieve efficient close-packing (in the absence of guest) with the molecule located on a centre of inversion. Consequently, it would be of great interest to synthesise new systems with an odd number of central link atoms, since these could not achieve an ordered arrangement located on a point of $\bar{1}$ symmetry.

5.4 Attempted Synthesis of 1,2-Diaryldisilane-based Systems

Silicon chains with *gem* dimethyl groups on the silicon atoms, provide much more bulk between the two aromatic rings. It was hoped that this might impart a little more rigidity into the chain and so reduce the number of ways in which the persubstituted molecule might pack, hence aiding the molecule's clathration ability.

With this in mind it was attractive to synthesise such molecules (187), and a suitable starting material appeared to be bis(pentachlorophenyl)-

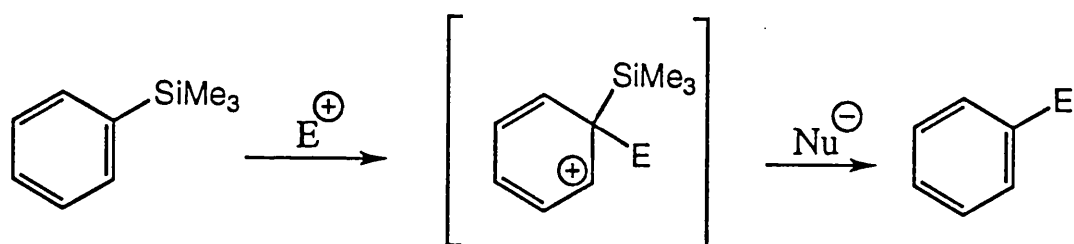
1,1,2,2-tetramethylsilane (186). It was hoped to prepare the desired molecules by reaction of the disilane (186) with appropriate thiolate nucleophiles under similar conditions to those used to synthesise the already described decasubstituted diphenylethanes (Scheme 31)



Scheme 31

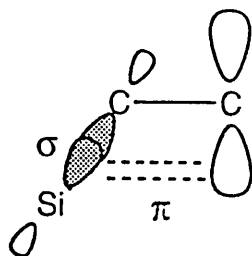
However, when the reaction was carried out under these conditions, using sodium phenylthiolate, the product obtained was not the decasubstituted disilane **(187)** but pentakis(phenylthio)benzene **(188)**. This is noteworthy in that these are nucleophilic conditions and normally aromatic desilylations occur under electrophilic conditions.

Under electrophilic conditions²²⁶ attack occurs at the ring carbon carrying the silyl group, that is at the *ipso*-position, because of the stabilisation of the adjacent carbonium ion, the β -effect (Scheme 32).

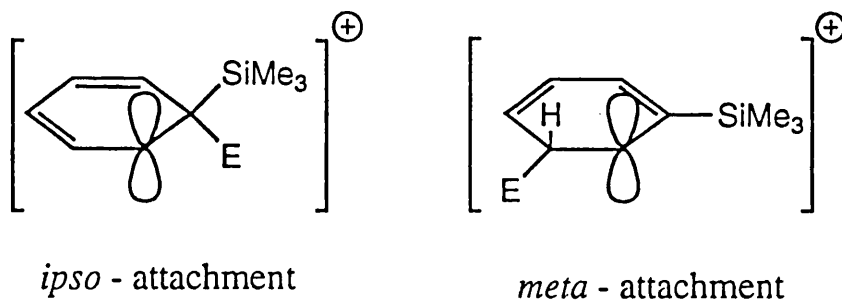


Scheme 32

This is due to the (p- Π) conjugation between the silicon-carbon bond and the developing positive charge in the transition state for the reaction.



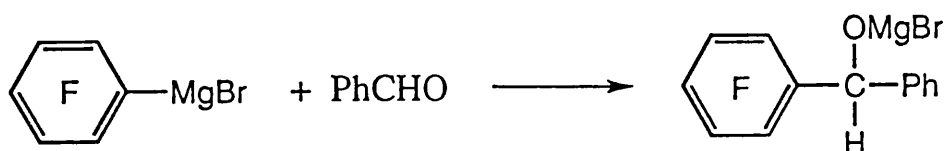
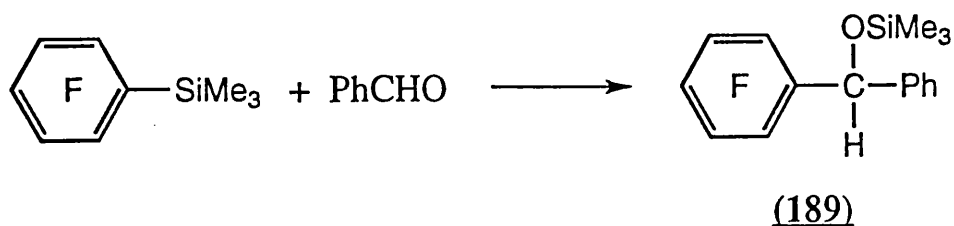
This overlap cannot be achieved if, say, electrophilic attack occurs at the *meta*-position as the orbitals involved are orthogonal to one another.



There have only been a few cases of nucleophilic desilylation reported, for example, aromatic silanes with electron withdrawing groups²²⁷ attached, either substituted on the ring or as an arene(tricarbonyl)chromium complex²²⁸, have been shown not to react with electrophiles unless there is the presence of a nucleophilic catalyst.

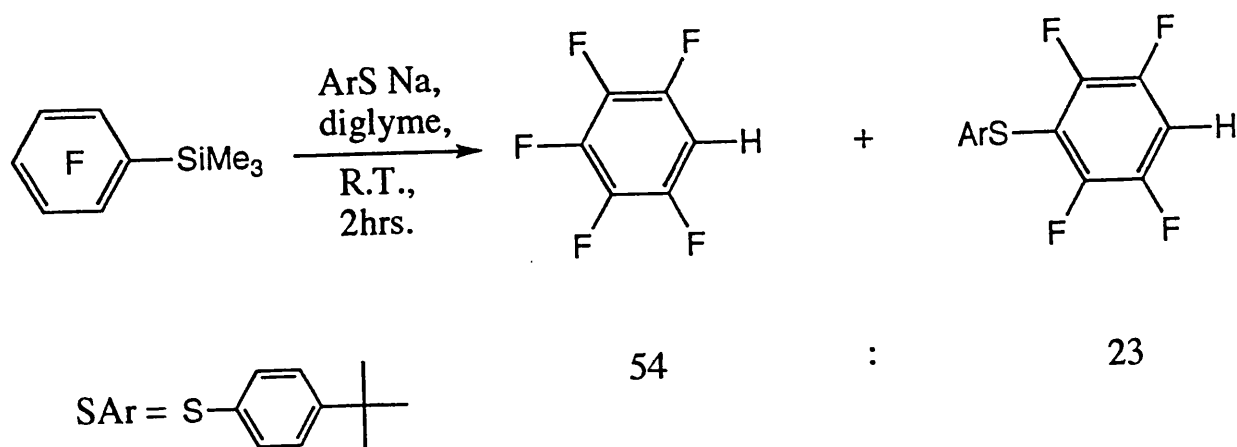
Perhaloarylsilanes, themselves, partake in some reactions characteristic of C-Metal bonds, for example, $C_6F_6SiMe_3$ reacts with benzaldehyde to give the trimethylsiloxy derivative (189)²²⁹ (c.f. the corresponding Grignard

reaction) (Scheme 32). It should be noted that no reaction is observed for the non-halogenated molecule phenyltrimethylsilane itself.



Scheme 33

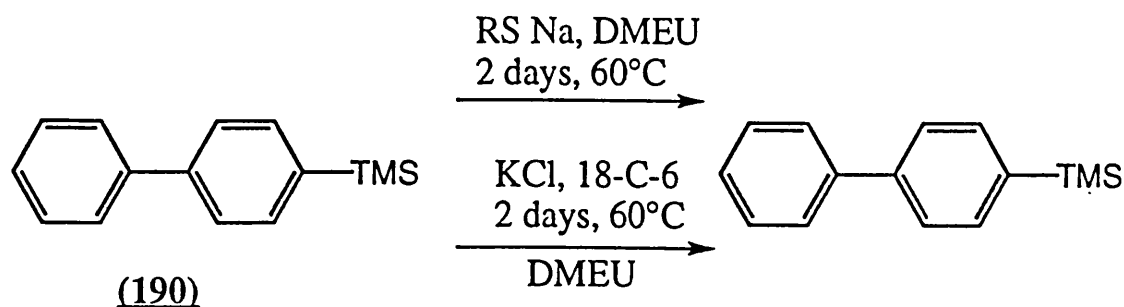
Bardin and co-workers have also described²³⁰, that under nucleophilic conditions, perfluorophenyltrimethylsilane is desilylated upon reaction with sodium *p*-*t*-butylphenylthiolate, in diglyme, the mixture of products formed being pentafluorobenzene and the *p*-substituted product shown (Scheme 34).



Scheme 34

This is very similar to the reaction we observed here and could give indications as to the possible mechanism of the present reaction. There are two major differences between the present reaction and that described by Bardin. The first is that we have desilylated a diaryltetramethyldisilane as opposed to an aryltrimethylsilane; and the second is that in the present reaction of (186) full substitution of all halogens by PhS- groups has occurred; this could be due to the increased reaction time, solvent and temperature. It was then decided to examine this interesting reaction in a little more detail.

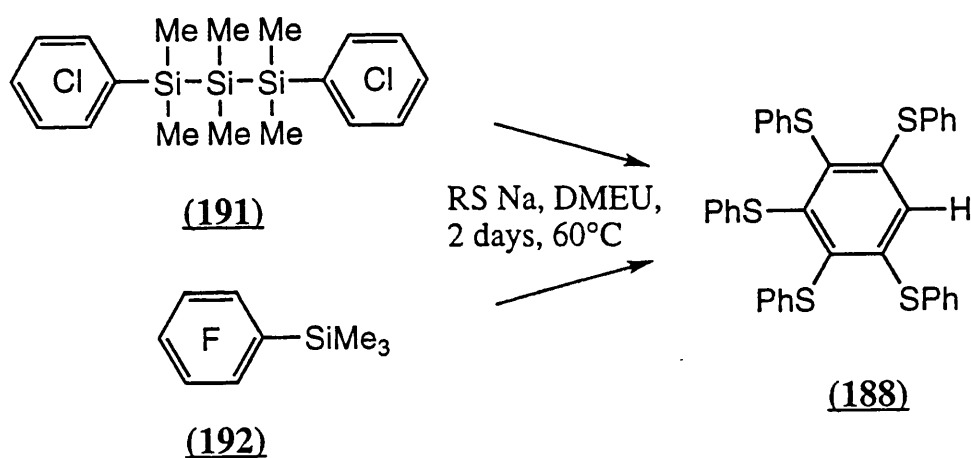
The first question addressed was: would the reaction take place in the absence of strong electron withdrawing groups on the phenyl ring? To throw light on this point biphenyltrimethylsilane (190), was prepared by reaction of the Grignard of 4-bromobiphenyl with trimethylsilyl chloride. When (190) was subjected to the reaction conditions used previously no reaction occurred and only starting material was recovered, as did the reaction of (190) with KCl and 18-crown-6, (18-C-6) (Scheme 35).



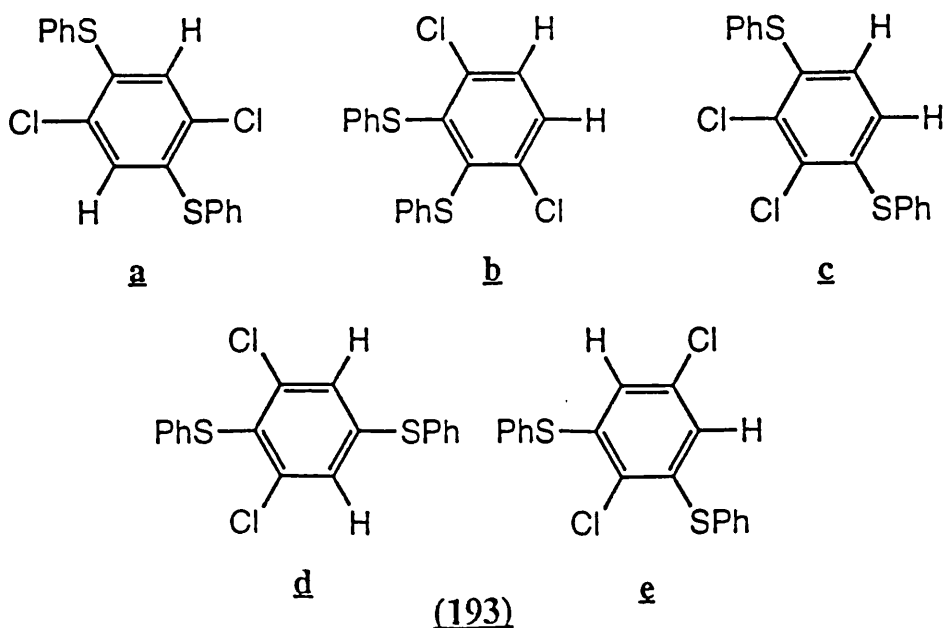
Scheme 35

This suggests that, somehow, the electron-withdrawing substituents are involved in the mechanism, for example, in stabilising an anion.

If this reaction is similar to Bardin's then other silanes should also be removed. With this thought in mind bis(pentachlorophenyl)-1,1,2,2,3,3-hexamethyltrisilane (**191**) and pentafluorophenyltrimethylsilane (**192**) were reacted under the same conditions (Scheme 36). Both of these gave the pentasubstituted benzene (**188**) observed before.



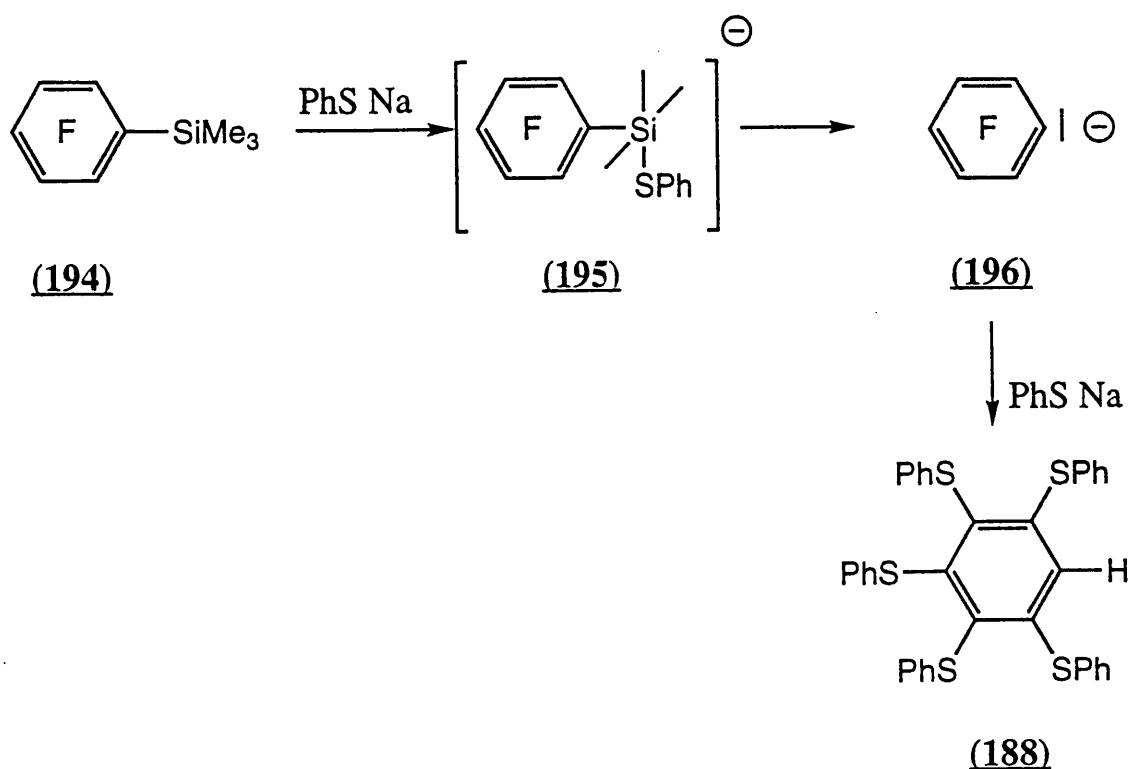
Scheme 36



From the reaction of the trisilane another product was isolated. From ^1H NMR and M.S. this product appears to be a dichlorodi(phenylthio)benzene (193). From the ^1H NMR spectrum one observes two isochronous protons on the central benzene ring. This gives, discounting chance isochrony, 5 possible structures (193a-e).

Although no unique structure could be assigned to (193) a strong peak at 872 cm^{-1} in the I.R. spectrum suggests two *meta* or *para* hydrogens on the central benzene ring, i.e. either (193a,d or e). This second product is probably formed from an impurity present in the trisilane (191) (^1H NMR shows the presence of aromatic protons in the starting material). The lack of one chlorine on the phenyl rings results in slower nucleophilic aromatic substitution and hence the isolation of the disubstituted product, the formation of which indicates that the silicon can be removed before full substitution has occurred.

From this evidence the following mechanism for the reaction was proposed (Scheme 37).



Scheme 37

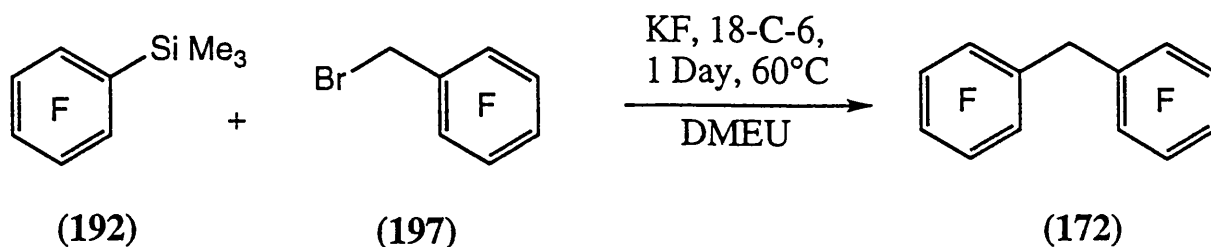
According to this mechanism, the nucleophile attacks the silicon to give a pentacoordinate silicon intermediate **(195)** which then gives anion **(196)** which is stabilised by the electron-withdrawing effects of the halogens. The anion then undergoes substitution and, ultimately, protonation. At present it is not known where the proton comes from. There seem to be four possible sources of the proton: H_2O , Si-CH_3 , SC_6H_5 and the solvent DMEU. The most acidic proton source is H_2O , which appears during the work-up; however, when the reaction was quenched with D_2O no loss of signal was

observed for the key proton NMR signal at δ 6.20, proving that this proton does not come from the water during work-up.

More work needs to be done to show from which of the other three sources the proton originates. Also, it is unknown at which stage of the substitution the anion is protonated. With replacement of the electron-withdrawing halogen groups by electron-donating phenylthio groups the lone pair is expected to become progressively more basic, hence more likely to abstract a proton from the surrounding environment.

If this mechanism is correct it suggests a way of synthesising linked pentafluorobenzenes, useful precursors to new potential linked hosts. With this in mind, it was decided to react pentafluorophenyltrimethylsilane (192) with an appropriate nucleophile, the fluoride anion, followed by quenching the reaction with an electrophile. Bardin²³¹ has already shown this to be done with electrophiles such as D_2O , Br_2 and so on.

Pentafluorobenzylbromide (197) was selected as the electrophile as this was expected to give bis(pentafluorophenyl)methane (172), an appropriate starting material for the preparation of $-CH_2-$ linked hosts (Scheme 38), assuming the above mechanism was correct.



Scheme 38

Reaction of (192) and (197) in the presence of potassium fluoride and 18-crown-6 indeed led to the isolation of (172), in an unoptimised yield of *ca.* 21%.

Although further work needs to be done on this reaction to optimise the yield, its occurrence shows that (192) can be used as a synthon for the pentafluorophenyl anion. This reaction, therefore, has potential as a source of novel linked hexa-hosts.

5.5 Pentasubstituted benzenes

A single-crystal X-ray analysis of the reaction product of **(186)** with PhSNa, **(188)** (Fig. 91) shows that the pentakis(phenylthio)benzene molecule adopts two different conformations in the unit cell. If one adopts the same notation as before and now introduces a new term **p** as a leg orientation in which C(core)-S-C(leg) plane is roughly defining the plane of the core, then the two conformations observed are **pabap** and **pbaap**. The crystals are triclinic (space group $P\bar{1}$).

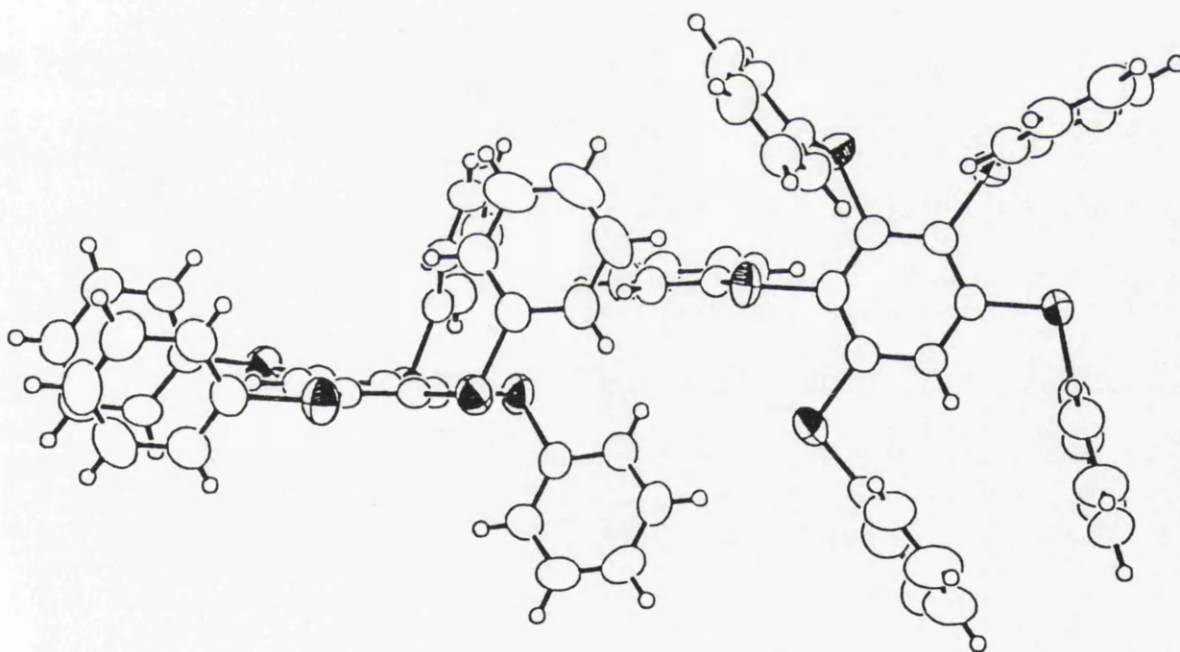
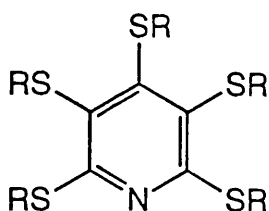


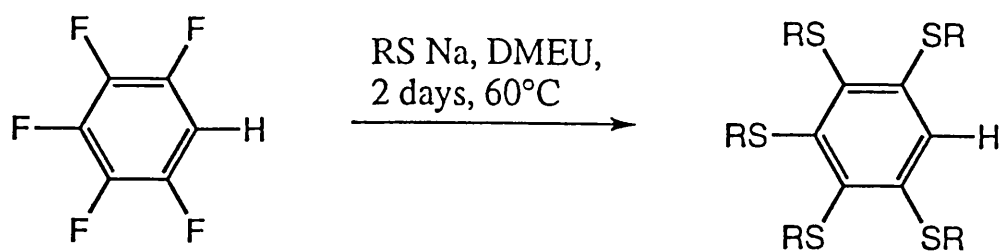
Fig. 91 The two crystallographically independent molecules observed in the molecular crystal pentakis(phenylthio)benzene **(188)**.

Pentakis(arylthio)pyridines (198) are, interestingly very similar structurally to their penta-substituted benzene analogues. Of the many pentasubstituted pyridines studied so far, only pentakis(*p*-methylphenylthio)pyridine has shown any tendency to form inclusion compounds. It was decided to investigate whether pentasubstituted benzenes would mimic the pentasubstituted pyridines in this behaviour or, would show improved inclusion ability.



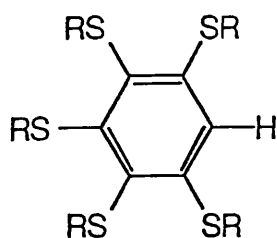
(198)

The required pentasubstituted benzenes were prepared by the conventional route, that is, reaction of the appropriate sodium thiolate with pentafluorobenzene (Scheme 39).



Scheme 39

Initially pentakis(phenylthio)benzene (188) was synthesised by this route to unambiguously prove that the product from the silane compounds also had this structure. Other pentasubstituted benzenes were then prepared (Table 13).



SR	SR
<p>(188)</p>	<p>(201)</p>
<p>(199)</p>	<p>(202)</p>
<p>(200)</p>	<p>(203)</p>

Table 13 Structures of pentasubstituted benzenes (188),(199)-(203), prepared from pentafluorobenzene.

As mentioned previously, pentakis(*p*-methylphenylthio)pyridine was the only member of the pentasubstituted pyridines that showed any ability to form inclusion compounds accordingly its close isosteric counterpart pentakis(*p*-methylphenylthio)benzene (199) was prepared. Contrasting the

behaviour of the pyridine and benzene series (199) failed to form inclusion complexes with either 1,4-dioxane or cyclohexane. We, therefore, decided to synthesise other pentasubstituted benzenes.

Compound (200)-(203) were prepared analogously and purified by gravity column chromatography. Further purification for (200) and (201) was achieved by recrystallisation from diethyl ether/hexane; chloroform/methanol, respectively.

Compounds pentakis(*p*-*t*-butylphenylthio)benzene (200), prepared to examine the effect of a bulky *para*-substituent and pentakis(3,5-dimethylphenylthio)benzene (201), to investigate the effect of *dimeta*-substitution, (known to be favourable in other systems) disappointingly yielded clear, colourless unsolvated crystals in each case.

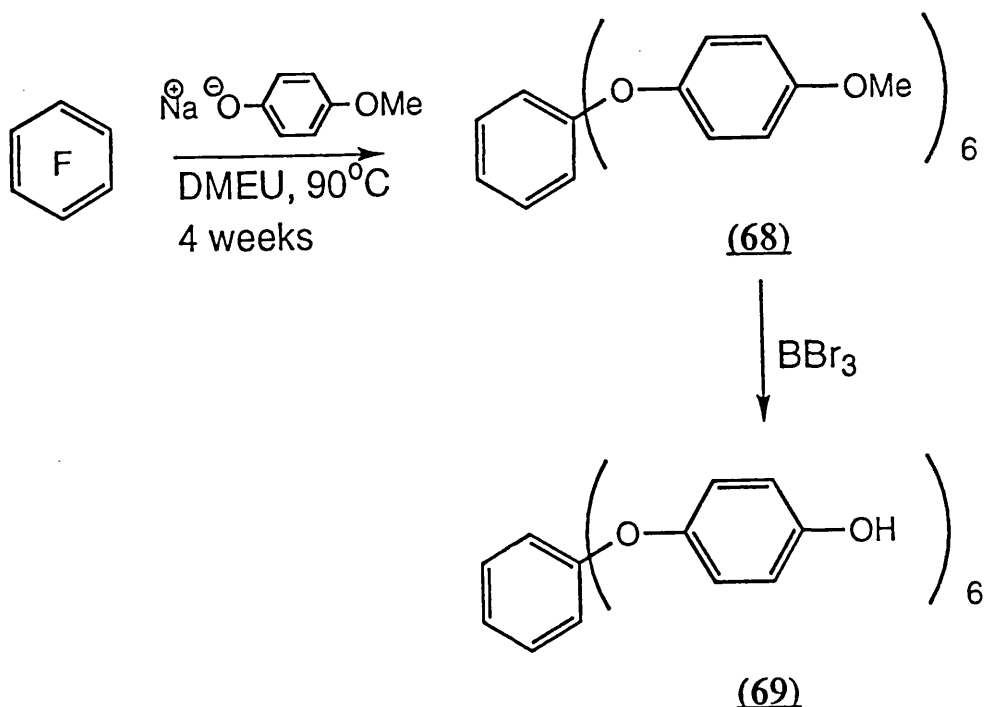
The effect of a cycloalkyl side-chain, as for, pentakis(cyclohexylthio)benzene (202) was then studied. (202) gave only an unsolvated white powder whilst the apparently attractive bulky chiral pentakis(10-*S*-camphorthio)benzene (203) was prepared for the two reasons of (a) chirality and (b) less tendency to adopt a near co-planar arrangement of either of the two legs adjacent to the central benzene hydrogen, due to steric effects. Compound (203), characterised by ^1H , ^{13}C NMR, was also obtained as an unsolvated white powder.

Although this is not a complete study, when one starts to compare pentasubstituted and hexasubstituted benzenes one can see that there is a total elimination of clathrate forming ability, for example, pentakis(phenylthio)benzene (188) does not include any guest whilst hexakis(phenylthio)benzene (58) includes CCl_4 and other guest species. This is due to an increase in flexibility caused by removal of one of the side-chain substituents, which allows the molecule to adopt a more compact conformation that can close pack in the solid state without the need for a guest molecule.

5.6 Hexakis(*p*-hydroxyphenoxy)benzene

Turning briefly from the successful strategies discussed above namely either using fused central cores as for anthracene or triphenylene based systems or by linking together hexa-host units, which has already demonstrated to be successful for one atom-linked molecules, novel results for a unique hexa-host are discussed. As has already been discussed in Chapter One β -hydroquinone is built up of two interlocking networks which are not linked to one another (in each network the molecules are bound together through hydrogen-bonded hexamers. Substantial quantities of hexakis(*p*-hydroxyphenoxy)benzene were prepared by reacting perfluorobenzene with sodium *p*-methoxyphenolate in DMEU, at 80°C, for

4 weeks (Scheme 40) and then reacting the resulting hexakis(*p*-methoxyphenoxy)benzene (68) with BBr₃.



Scheme 40

The structure with pyridine as the guest has already been discussed in the introduction, however recent results, unpublished at the time of writing have revealed structural characteristics of a second type of adduct which also has space group *R*3 with unit cell dimensions *a* = 15.3253(9) Å and *c* = 26.077(7) Å determined by powder X-ray studies. CPMAS NMR studies carried out parallel to the present study indicate that the methanol clathrate and the hydrate (obtained from moist ethanol) have the same structure. The structure of the latter has been unambiguously determined by single crystal X-ray diffraction (Fig. 92). The water molecule guest is not shown in this

figure. As can be seen from Fig. 92 there are two interpenetrating host lattices, not connected and these are enantiomerically related. The situation is directly analogous to β -hydroquinone but whereas the cavity length of β -hydroquinone is *ca.* 5-6 Å, because of the van der Waals thickness of the benzene ring there are three types cavity with lengths *ca.* 3, *ca.* 4.5 and *ca.* 6 Å. The 6 Å cavity is similar to β -hydroquinone, that is, between two $[\text{OH}]_6$ hexamers. The 4.5 Å cavity has ends comprised of a $[\text{OH}]_6$ hexamer and a benzene ring, whilst the 3 Å cavity is bounded by two benzene rings. Analogously to β -hydroquinone ethanol is too large to be bound into any of the cavities. Accordingly this was chosen as a solvent for hydrogen inclusion studies. The reason that this structure was investigated for hydrogen inclusion was that the potential escape route for hydrogen along the *c* axis direction through the $[\text{OH}]_6$ hexamers in β -hydroquinone was blocked by the benzene rings in (69). (69) and ethanol were, therefore, placed into a bomb and this was put under an atmosphere of hydrogen at a pressure of 15,000 p.s.i. and heated to 200°C with shaking. After 15 hrs the bomb was allowed to cool to room temperature and left for one week to recrystallise to give a white crystalline material.

Three runs were carried out which used as the solvent (a) absolute ethanol as supplied, (b) dried ethanol (using Mg turnings) and (c) 5% water added to the ethanol. For runs (a) and (c) hydrogen was detected by mass spectrometry (thanks to Dr. R. Anderson, Forensic Science, Glasgow University). For run (b), however, no hydrogen was seen indicating that

water may play a potential roll in inhibiting diffusion of the hydrogen, possibly by preventing motion in the *ab* plane.

A slightly larger gas molecule was then investigated with the hope that (69) would store this guest more perminately. Hydrogen sulphide was the gas chosen, this had the added advantage of if it was included in (69) then the resulting clathrate should be more stable than the hydrogen sulphide clathrate of β -hydroquinone. (69) was dissolved up in benzyl alcohol and after hydrogen sulphide has been passed through the solution toluene was added to precipitate out (69). The resulting white powder, however showed no signs of inclusion of the guest, as indicated by microanalysis. If more time had been available it would be worth investigating the inclusion of hydrogen sulphide at high pressure.

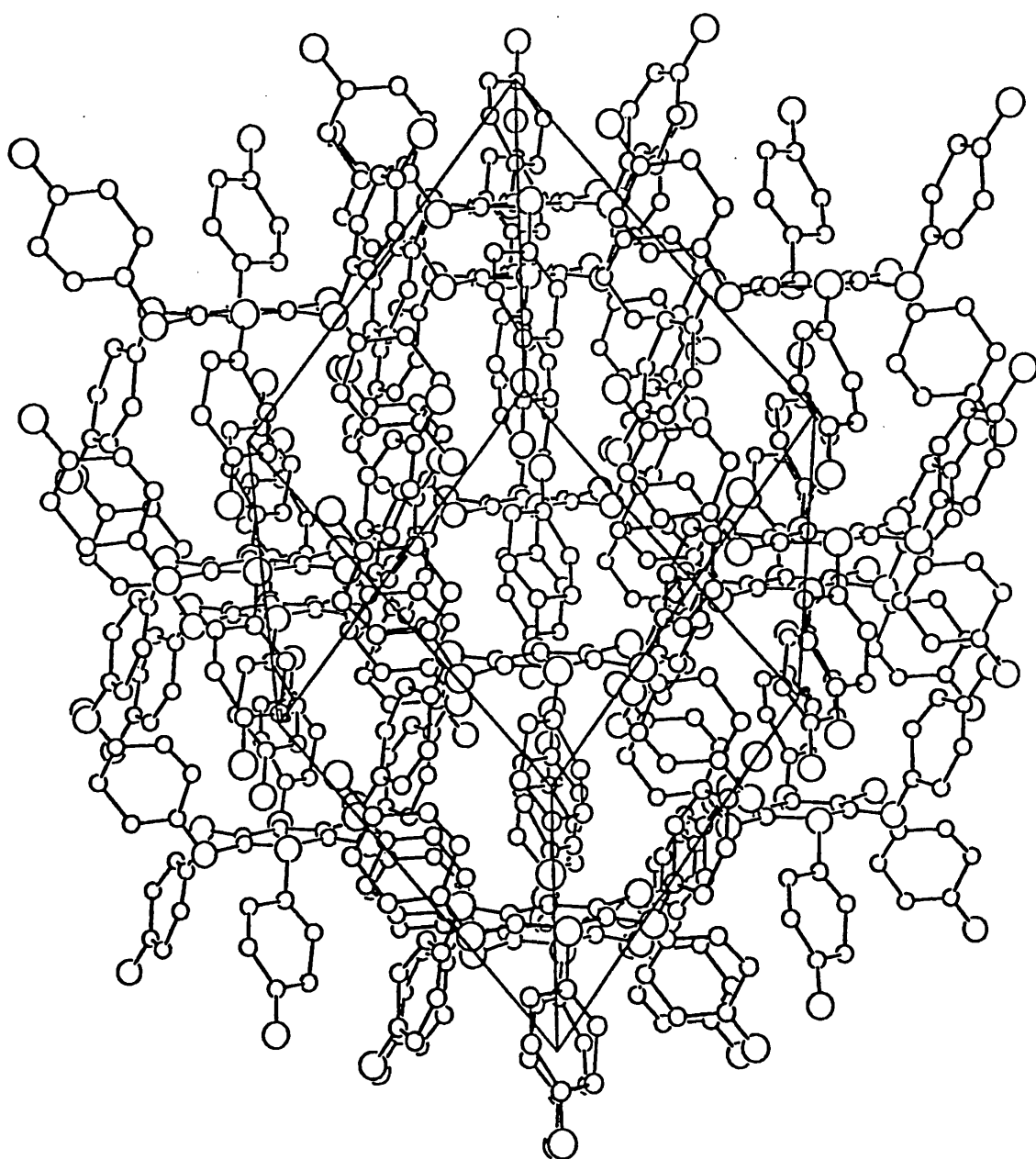
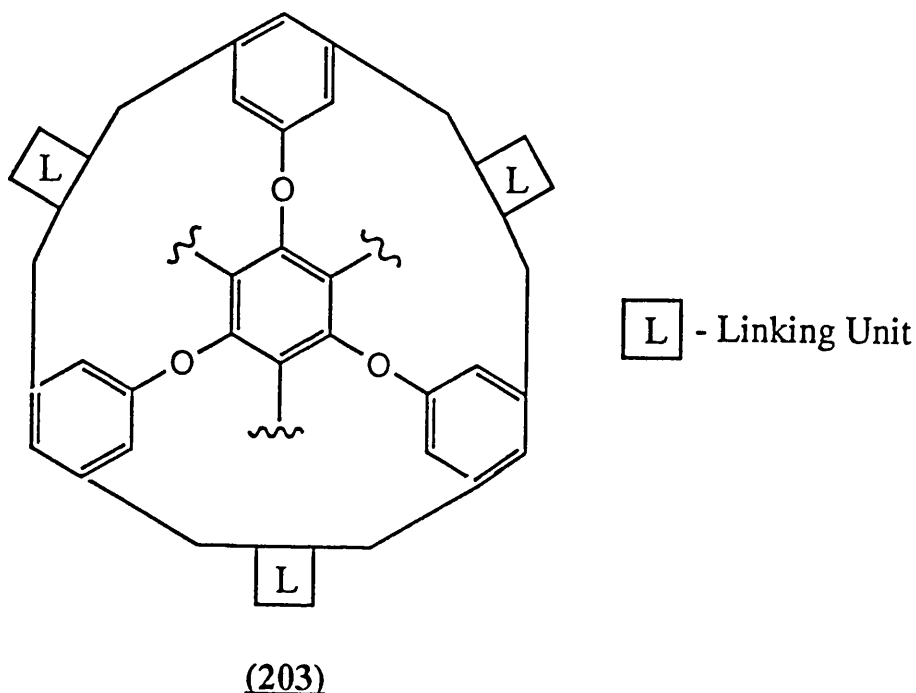


Fig. 92 Molecular architecture of the hexakis(*p*-hydroxyphenoxy)benzene hydrate. The water molecule is not shown here.

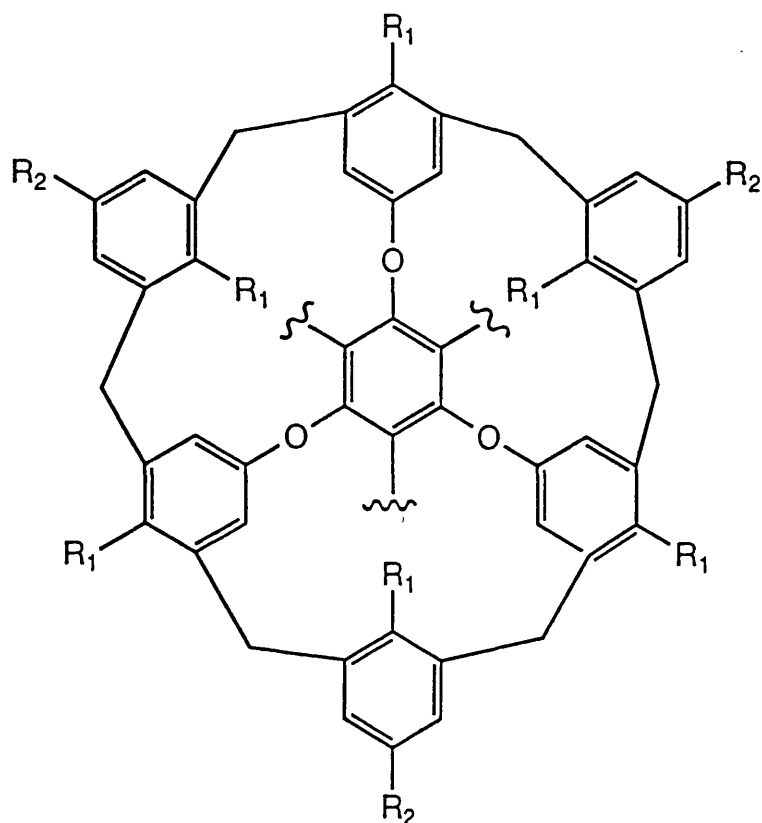
5.7 Attempted Linking of Side-chain Units of Hexasubstituted Benzenes

In order to extend the idea of a greater degree of preorganisation of the side chain moieties hexa-host molecules of the type (203) were targeted. The synthesis of these required linking of the 'arms' (or side-chains) of a hexa-substituted benzene to give the double-ended basket.



The first linking units tried were aromatic entities *meta* linked to the original side-chain units by methylene groups since these would ensure a rigid preorganised structure, as shown by molecular models, general formula (204). Because of potential synthetic accessibility, compound (205) was selected particularly in view of calixarene chemistry. It is well known that calixarenes can be synthesised by a variety of base or acid catalysed reactions of formaldehyde with *p*-substituted phenols²³². Therefore, it was

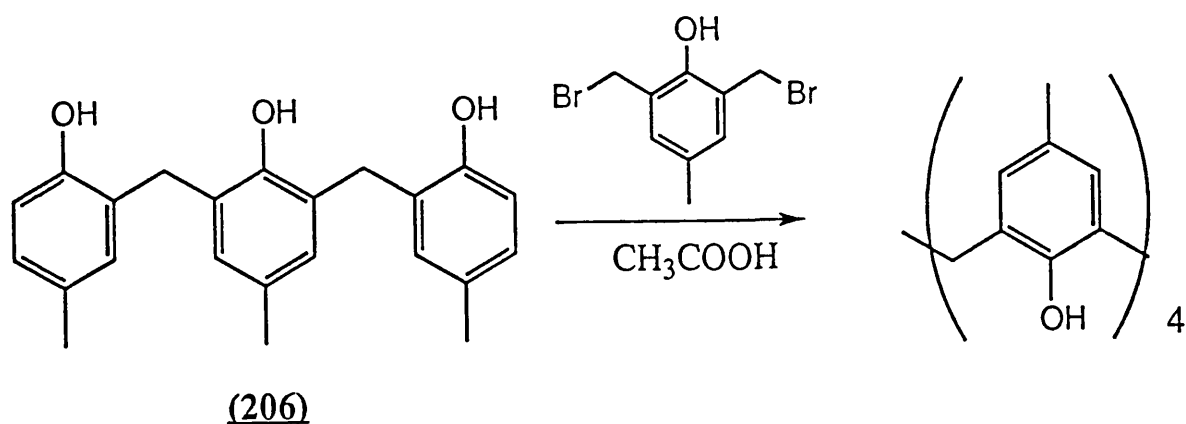
hoped to use hexakis(*p*-hydroxyphenoxy)benzene (69) as the *p*-substituted phenol and then link it, with the appropriate units.



(204) : $R_1 = R_2 = H$

(205) : $R_1 = OH$; $R_2 = Me$

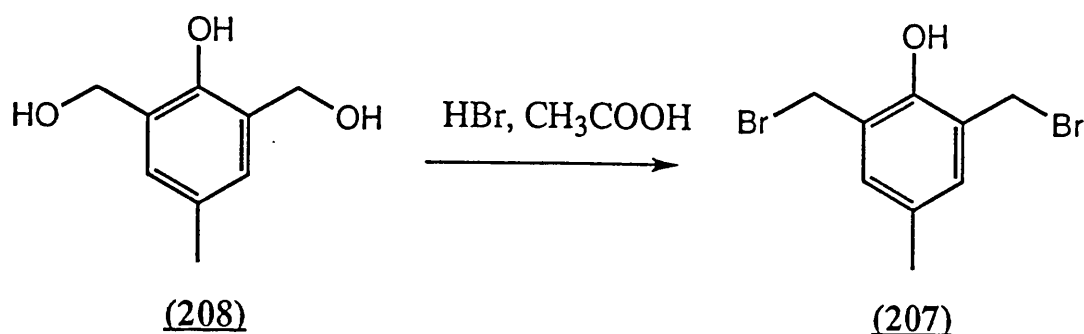
Bohmer and co-workers have shown that calixarenes can be synthesised by convergent step-wise reactions with the final cyclisation process occurring when triphenol (206) is reacted with 2,6-bis(bromomethyl)-*p*-cresol (207) in acetic acid (Scheme 41)²³³.



Scheme 41

Accordingly an attempt to link hexakis(*p*-hydroxyphenoxy)benzene with 2,6-bis(bromomethyl)-*p*-cresol was made under similar conditions.

The required building block 2,6-bis(bromomethyl)-*p*-cresol (**207**) was synthesised²³⁴ by reacting HBr/acetic acid with 2,6-bis(hydroxymethyl)-*p*-cresol (**208**) (Scheme 42) in a yield of *ca.* 66%.



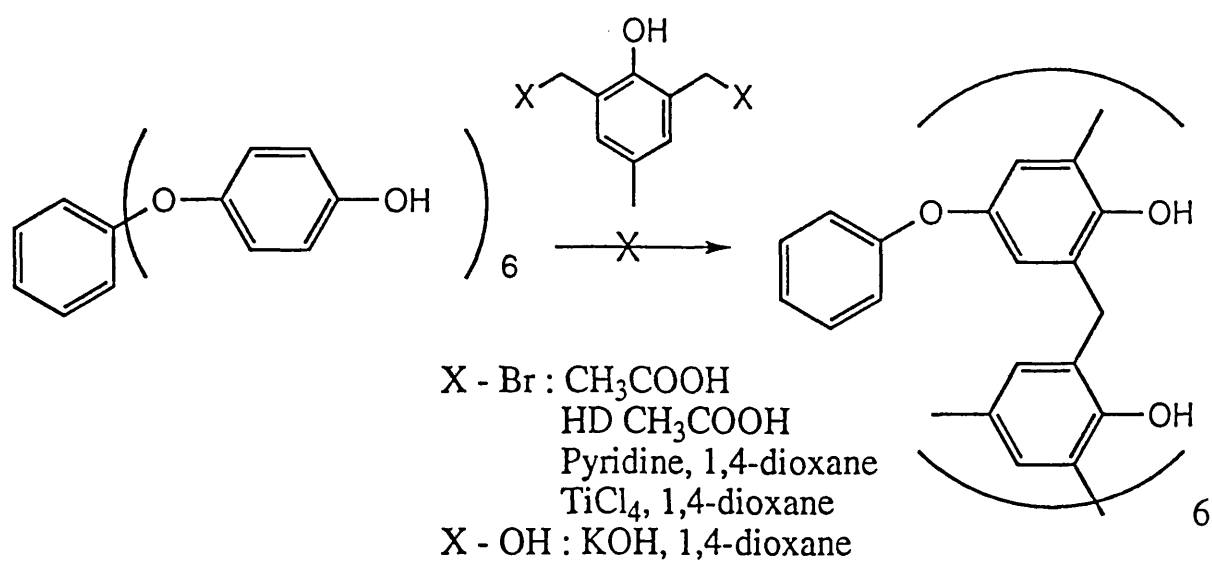
Scheme 42

(207) was then added over a period of 4 hours to a refluxing mixture of acetic acid and hexaphenol (69) (Scheme 43). After a further 48 hrs the mixture was worked-up to give a green solid from which no isolatable products could be obtained. High dilution techniques were then tried, with acetic acid as the solvent, however, again no products could be isolated.

TiCl₄ has been shown to give better ring closure yield for the reaction in Scheme 40 without the need for high dilution techniques²³⁵. (69) was, therefore, reacted with dibromide (207) in the presence of TiCl₄ in dry 1,4-dioxane, however, as before no isolatable products were obtained.

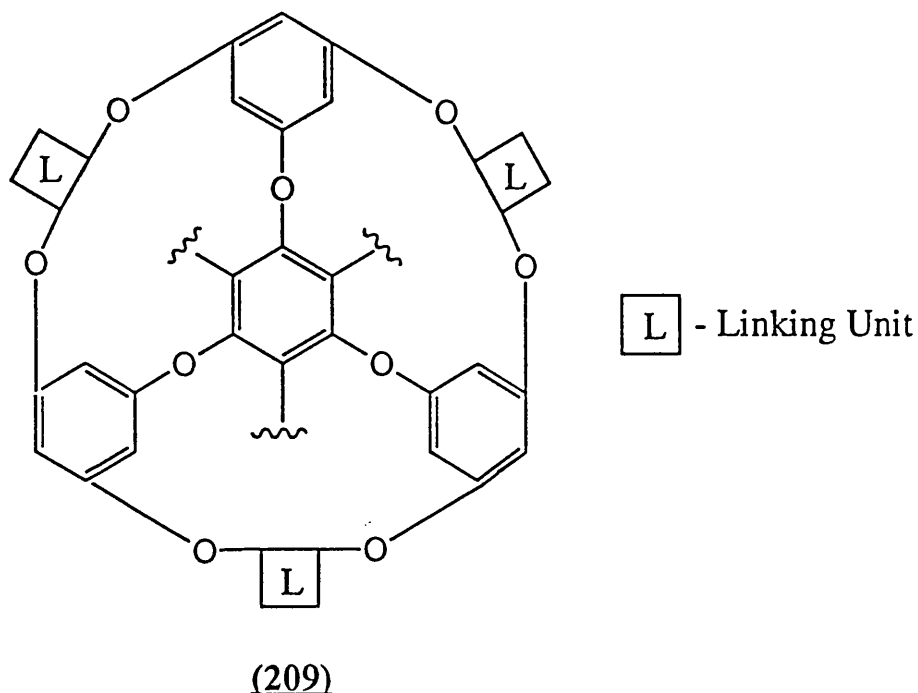
Finally, as calixarenes can be formed under basic conditions^{236,237}, 2,6-bis(hydroxymethyl)-*p*-cresol (208) was reacted with hexaphenol (69) and

KOH in xylene using a Dean-Stark apparatus to remove any water formed in the reaction, but again no pure products could be isolated.

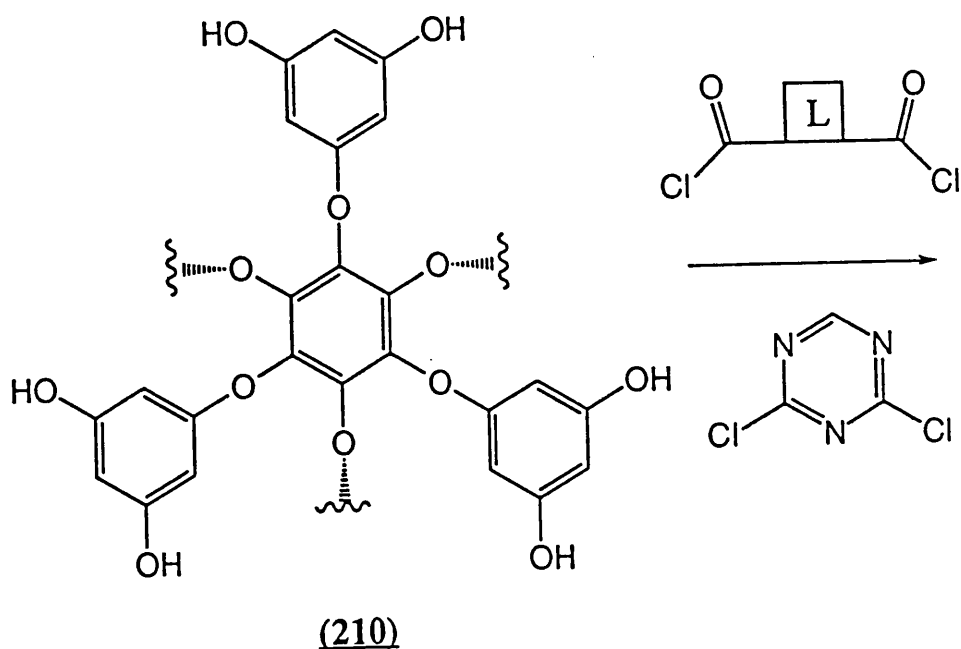


Scheme 43

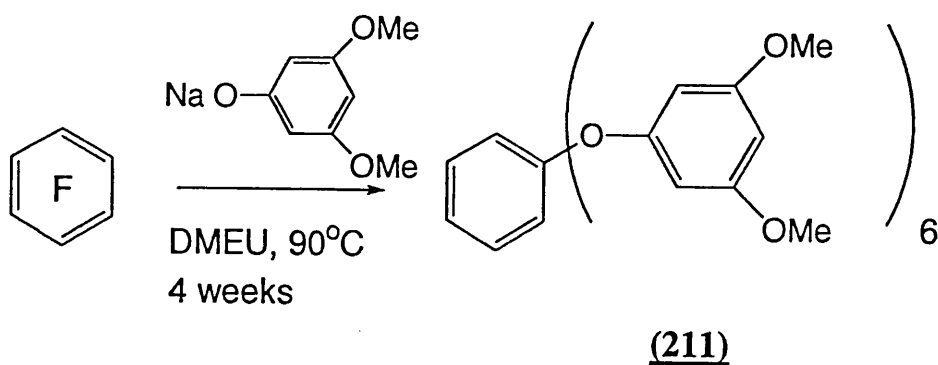
Following the disappointing failure of this ring closure procedure another target molecule **(209)** was selected.



This target molecule appeared accesible by reacting hexakis(3,5-dihydroxyphenoxy)benzene **(210)** with either a diacid chloride (esterification) or a dichloroaromatic (nucleophilic substitution) (Scheme 44).



Scheme 44



Scheme 45

It was proposed to synthesise (210) by demethylation of hexakis(3,5-dimethoxyphenoxy)benzene (211). The latter was prepared by reacting sodium 3,5-dimethoxyphenolate with hexafluorobenzene for 8 weeks, in DMEU, at 80°C (Scheme 45) to give beautifully crystalline (211). (211) shows no propensity to include. The X-ray structure shows that one methoxy of each arm points into the centre of the molecule (Fig. 93) and so inhibits clathrate formation. This shows the need for preorganisation of this host to give a preformed cavity. The crystals are triclinic (space group $P\bar{1}$) and the molecule adopts two crystallographically distinct conformations both of which are centrosymmetric.

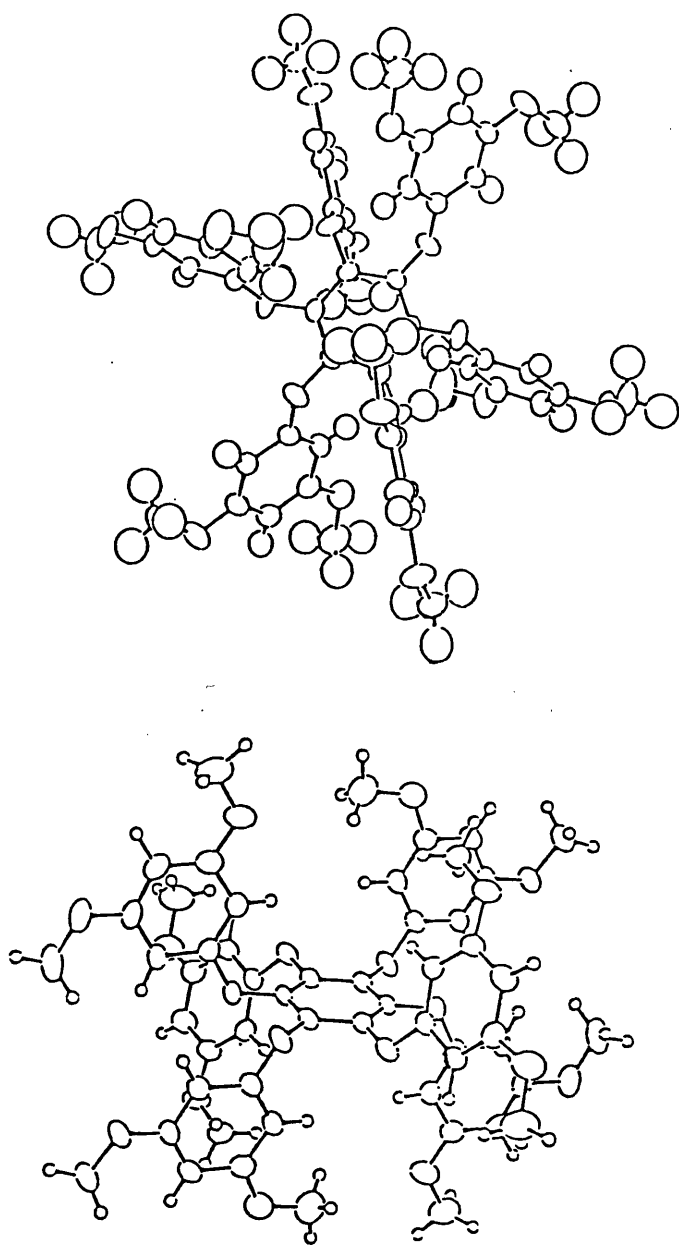


Fig. 93 Conformation of (211) in its molecular crystal (two crystallographically independent molecules).

When, however, demethylation of (211) by BBr_3 was tried no product was isolated. The problems observed here could be possibly due to the fact that BBr_3 has been known to only monodemethylate some 3,5-dimethoxybenzenes²³⁸. Demethylation was then tried with pyridinium chloride but, as before, no product could be isolated. This was attributed to the water solubility of the target product, which has 12 hydroxy groups

rendering it difficult to isolate. A way round this could be to quench the reaction with an acylating reagent e.g. acetyl chloride thus forming the dodeca-acetate of (212). This should be more soluble in organic solvents and so making it easier to isolate. Unfortunately, due to lack of time this was not tried.

EXPERIMENTAL

GENERAL PROCEDURES, INSTRUMENTS

AND SELECTED MATERIALS

Melting points (m.pt.) were determined on a Kofler hot-stage apparatus and are uncorrected. Infra-red spectra were recorded on a Perkin-Elmer 983 spectrophotometer as potassium bromide discs (unless otherwise stated). The following abbreviations are used : s-strong; m-medium; w-weak; br-broad.

Proton nuclear magnetic resonance (NMR) spectra were determined on a Perkin Elmer R32 (90 MHz) and Varian EM390 (90 MHz) spectrometers using tetramethylsilane (TMS) as internal standard and Brüker AM200SY (200 MHz) and Brüker WP200SY spectrometers using the deuterated solvent as reference signals. Carbon NMR spectra were determined on the latter two instruments at 50 MHz ; signals relative to the deuterated solvent and proton noise decoupled. The fluorine NMR spectrum was determined on the Brüker AM200SY (188 MHz) spectrometer using CFCl_3 at 0 ppm as the internal standard. The following abbreviations are used: s-singlet; d-doublet; t-triplet; q-quartet; and m-multiplet.

Routine mass spectrometry (<900 amu) was determined using a VG/Kratos M12 spectrometer. Mass spectrometry for compounds >900 amu

was provided by the SERC fast atom bombardment (FAB) mass spectrometry service, Swansea College.

All microanalyses were determined on a Carlo Eerba elemental analyser, model 1106.

Column chromatography was performed using Fluka Kieselgel HF₂₅₄ and, for flash chromatography Merck Kieselgel 60 230-400 mesh. Preparative thin layer chromatography (TLC) was performed using 20 x 20 cm glass precoated with 2mm of Merck Kieselgel 60 F₂₅₄ (No. 5717). Qualitative reverse-phase TLC was performed using Macherey-Nagel Duren nanosilica C18 100UV₂₅₄ 0.20mm plates. Merck 0.2mm precoated aluminium foil (No. 5554) was also used.

THIOL SYNTHESIS

1. Preparation of O-(*p*-cumylphenyl)dimethylthiocarbamate.

To a cooled solution of *p*-cumylphenol 15g (0.0708 moles) in 150 ml of dry dimethylformamide (DMF) contained in a 500 ml 3-necked flask equipped with a condenser and nitrogen bleed, was added in small quantities, 95% sodium hydride 2.15g (0.085 moles). The cooling bath was removed and the mixture stirred under a continuous nitrogen flow until no further bubbles were observed. Dimethylthiocarbamoyl chloride 10.817g (0.088 moles) was then added and the reaction temperature raised to 80°C. The mixture was stirred under nitrogen for a further 2 hours, it was then added to 300 ml of water in a separating funnel and extracted twice with toluene (150 ml). The combined extracts were then washed with 5-10% potassium hydroxide solution (400 ml) and saturated sodium chloride solution (400 ml). The solution was then dried over magnesium sulphate and filtered. Upon concentrating to dryness and recrystallisation from methanol 10.54 g (49.8% yield) of pure white material was obtained. m.pt. 112-113°C; δ_{H} (90 MHz, CDCl_3) 7.32-6.92 (m, 9H, ArH), 3.45(s, 3H, C(S)NCH₃), 3.30 (s, 3H, C(S)NCH₃), 1.69(s, 6H, ArC(CH₃)₂Ar); m/e 299, M⁺.

2. Preparation of S-(*p*-4-cumylphenyl)dimethylthiocarbamate

Pure dry O-(*p*-4-cumylphenyl)dimethylthiocarbamate 10g (33.4 mmoles) was heated in a flamed dry pyrolysis tube at 275°C in a Wood's metal bath for 1.5 hours. The resultant pale yellow gum was then recrystallised from methanol giving 8.26g of the S-aryl compound as colourless needles, yield 82.6%; m.pt. 102-103°C; δ_{H} (200 Hz, CDCl_3) 7.30-7.12 (m, 9H, ArH), 3.05 (s, 6H, $\text{C}(\text{O})\text{N}(\text{CH}_3)_2$), 1.67 (s, 6H, $\text{ArC}(\text{CH}_3)_2\text{Ar}$); m/e 299 M^+ .

3. Preparation of *p*-cumylthiophenol (114)

60 ml of methanol was purged with nitrogen. It was then added to a 3-necked flask equipped with a stirring bar, condenser and nitrogen bleed. 7.6g (0.025 moles) of the S-aryl was added under a nitrogen flow. A 70 ml, 50% potassium hydroxide solution was then prepared and purged with nitrogen. Addition of the potassium hydroxide solution to the flask resulted in precipitation of the S-aryl from solution. The reaction mixture was refluxed under a nitrogen flow with vigorous stirring until the precipitate has disappeared (~ 2 hours). The mixture was refluxed for a further 30 minutes to ensure hydrolysis was complete. Cooling of the reaction mixture under a nitrogen atmosphere, followed immediately by addition of concentrated hydrochloric acid to pH 1, resulted in a yellow oily film being deposited on the surface of the solution. The reaction mixture was then transferred to a separating funnel containing 300 ml of water. Extraction of the thiol was accomplished using 2 x 200 ml of toluene. The organic extracts were then washed with brine, and concentrated to dryness under reduced pressure to give a yellow solid. Distillation of the crude thiol at 125°C 0.005mm gave 4.57g (78.9% yield) of a white crystalline material. m.pt. 43-44°C. δ_{H} (200 MHz, CDCl_3) 7.27-7.07 (m, 9H, ArH), 3.38 (s, 1H, ArSH), 1.64 (s, 6H, $\text{ArC}(\text{CH}_3)_2\text{Ar}$); MS m/e 228 M^+ .

4. Preparation of O-(5-indanyl)dimethylthiocarbamate

Sodium 5-indanoxide was made from 5-indanol 20g (0.149 moles) and 95% sodium hydride 4g (0.158 moles) according to the method and conditions of Example 1. It was reacted at 80°C for 2 hours with dimethylthiocarbonyl chloride 22.8g (0.185 moles) and the reacted material also isolated according to the method of Example 1. Recrystallisation of the crude product from methanol gave 10.2g (25% yield) of the desired O-aryl compound m.pt. 68-70° C. Found: C, 64.98; H, 6.83; N, 6.24% $C_{12}H_{15}SNO$ requires C, 65.15; H, 6.79; N, 6.33%; δ_H (200 MHz, $CDCl_3$), 7.19 (d, $J=8Hz$, 1H, ArH), 6.89 (s, 1H, ArH), 6.79 (m, 1H, ArH), 3.42 (s, 3H, C(S)NCH₃), 3.29 (s, 3H, C(S)NCH₃), 2.89 (m, 4H, 2 x ArCH₂), 2.07 (quintet, $J=7.2Hz$, 2H, CH₂); ν_{max} (KBr disc) 2950(s), 2862 (w), 2840 (m), 1605(w), 1590 (w), 1535 (s), 1480 (s), 1436 (m), 1403 (m), 1391 (s), 1320 (w), 1285 (s), 1230 (s), 1170 (s), 1140 (s), 1078 (m), 1050 (w), 1000 (w), 962 (m), 911 (m), 902 (m), 855 (m), 825 (s), 703 (m), 670 (w) cm^{-1} ; MS m/e 221 M^+ .

5. Preparation of S-(5-indanyl)dimethylthiocarbamate

O-(5-indanyl)dimethylthiocarbamate 10.2g (0.046 moles) was heated in a flamed dried pyrolysis tube at 280°C in a Wood's metal bath for 3 hours. Crystallisation of the crude material from methanol gave 10.0g (98% yield) of the corresponding S-aryl, m.pt. 47-49°C. δ_H (200 MHz, $CDCl_3$) 7.34 (s, 1H, ArH), 7.23 (s, 2H, 2 x ArH), 3.04 (s, 6H, $C(O)N(CH_3)_2$), 2.90 (m, 4H, 2 x $ArCH_2$), 2.09 (quintet, 2H, CH_2); MS m/e 221 M^+ .

6. Preparation of 5-Indanethiol (115)

S-(5-Indanyl)dimethylthiocarbamate 10g (0.0452 moles) was hydrolysed using the same method and conditions of Example 3. Isolation of the product by the method of Example 3 gave a crude liquid, thiol. Distillation at 66-68°C / 0.005 mm gave 5.2g (76.7% yield). Found: C, 72.08; H, 6.40% $C_9H_{10}S$ requires C, 72.00; H, 6.66%; δ_H (200 MHz, $CDCl_3$) 7.37 - 7.01 (m, 3H, 3 x ArH), 3.38 (s, 1H, $ArSH$), 2.83 (m, 4H, 2 x $ArCH_2$), 2.03 (quintet, 2H, CH_2); ν_{max} 3050 (w), 3010 (m), 2942 (s), 2860 (m), 2840 (s), 2559 (m), 1597 (s), 1565 (m), 1472 (s), 1431 (s), 1405 (m), 1309 (w), 1302 (w), 1288 (w), 1257 (m), 1175 (m), 1100 (m), 1035 (w), 873 (m), 860 (m), 808 (s) cm^{-1} ; MS m/e 150 M^+ .

7. Preparation of Cyclohepta-1,3-dithiane

Cycloheptanone 44.8g (0.4 moles), 1,2-ethanedithiol 34.0 ml (0.41 moles) and p-toluenesulphonic acid monohydrate (1.30g, 6.8 mmoles) were dissolved in toluene (200 ml) and heated at reflux for 2 hours in a Dean-Stark apparatus, liberting *ca.* 7 ml of water at the completion of the reaction. The solution was cooled and washed with water (5 x 100ml), the organic layer was then dried with magnesium sulphate and filtered. Finally, the solution was evaporated to dryness under reduced pressure to give a yellow/orange oil which solidified when cooled to yield 72.74g (yield 96.73%); δ_{H} (90 MHz, CDCl_3) 3.3 (s, 4H, $\text{SCH}_2\text{CH}_2\text{S}$); 2.2-1.6 (m, 12H, 6 x CH_2); MS m/e 188 M^+ .

8. Preparation of Cycloheptathiol (116)

Cyclohepta-1,3-dithiane 43.24g (0.23 moles) was dissolved in dry ether (300 ml) and *n*BuLi 66ml (10M in hexane, 0.66 moles) was slowly added with stirring under a nitrogen flow while cooling the reaction vessel in an ice water bath. The reaction was allowed to warm to room temperature overnight. After 16 hours 250 ml of water was slowly added (Caution). A further portion of ether was added and the organic layer was washed with water (3 x 300ml) and then dried over MgSO_4 filtered and evaporated to dryness under reduced pressure to give the crude product 27.82g. This was then distilled at 74°C (15 mm) to give 17.2g (57.53%) of pure clear liquid. δ_{H} (90 MHz, CDCl_3) 3.1 (m, 1H, RSH), 2.2 (s, 1H, CHSH), 2.15-1.2 (m, 12H, 6 x CH_2); MS m/e 130, M^+ .

9. Preparation of (S)-10-Camphorsulphonyl Chloride

To a 1 litre 3-necked flask equipped with an overhead mechanical stirrer, was added (S)-10-camphorsulphonic acid 25g (0.108 moles) and phosphorous pentachloride 22.47g (0.108 moles). After some of the material had liquified the flask was placed in an ice-bath until the vigorous reaction had subsided. It was stirred vigorously until all the PCl_5 had dissolved and then poured onto crushed ice and then into a second beaker containing crushed ice and poured back and forth until the reaction was complete. The mixture was then filtered and the solid dried over phosphorous pentoxide. This yielded 13.92g (51.61%) of (S)-10-camphorsulphonyl chloride; MS m/e 250 M^+ .

10. Preparation of (S)-10-mercaptocamphor (118)

To a 3-necked flask was added glacial acetic acid 57 ml, red phosphorous 23g (0.74 moles) and iodine 2.02g (0.016 moles). The mixture was then heated and stirred vigorously. While at boiling (S)-10-camphorsulphonyl chloride 13.81g (0.055 moles) was added slowly, and then refluxed for four hours. Once the mixture had cooled water (10.5ml) was added very cautiously to prevent too rigorous a reaction occurring. The solution was then refluxed for two hours and then steam distilled. This was done by transferring the mixture into a round bottomed flask and initially 285 ml of water added, but altogether 885 ml, and then distilling the mixture. The thiol was extracted with pentane and recrystallised from hot ethanol and water to yield white crystals. 14.12g (69.6%) m.pt. 65-66°C. Found: C, 65.09; H, 8.79%; S, 17.52%, $C_{10}H_{16}SO$ requires C, 65.22; H, 8.69; S, 17.39%. δ_H (90 MHz, $CDCl_3$) 2.83 (dt, 1H, $CHHS$), 2.32 (m, 2H, $CHHS$, $C(O)CH$), 2.10-1.60 (m, 7H, 5 x alkylH, CH_2SH , $C(O)CH$), 1.00 (s, 3H, CH_3), 0.90 (s, 3H, CH_3): ν_{max} (KBr disc) 2988 (m), 2964(s), 2950 (s), 2928 (m), 2566 (w), 1733(s), 1412(m), 1389(m), 1376(m), 1326(w), 1298(m), 1281(w), 1071(m), 1048(m), 1030(m), 733(w) cm^{-1} .

11. (-)-O-Menthyl-S-1-phenylethylthiocarbonate

To (-)-menthol 10g (0.064 moles) dissolved in diethyl ether (50 ml) was added NaH (95%) 1.78g (0.070 moles) under N_2 and refluxed gently until all the NaH had reacted. Toluene (50 ml) was then added and the solution cooled. Carbon disulphide 4ml (0.07 moles) was added slowly through a dropper, and to the resulting orange solution 1-phenylethylbromide 10.36g (0.056moles) was added dropwise and refluxed for 4 hours, allowed to cool down to room temperature and stirred overnight. The resulting solution was washed with water and dried (Na_2SO_4). Removal of the solvent gave an oil. Addition of ethanol (80 ml) gave a white crystalline precipitate which was filtered and recrystallised from ethanol until $[\alpha]_D$ was constant to yield 3.94g of optically pure material m.p. 76-77°C; $[\alpha]_{589} = 161.8^\circ$ ($c=2.01$, C_6H_6); δ_H (200 MHz, $CDCl_3$) 7.39 - 7.19 (m, 5H, ArH), 5.51 (td, $J=10.7$, 4.5 Hz, 1H, $RCHOC(S)S$), 4.86(q, $J=7$ Hz, 1H, $ArCH(CH_3)S$), 2.75 (m, 1H, alkylH), 1.70-1.47 (m, 8H, alkylH), 1.26-0.71 (m, 12H, alkylH); δ_C (50 MHz, $CDCl_3$), 212.62(s), 142.10(s), 129.56(d), 127.38(d), 127.30(d), 84.09(d), 48.77(d), 47.15(d), 39.73(t), 34.08(t), 31.35(d), 26.09(d), 23.41(t) 21.96(q), 20.73(q), 16.64(q); ν_{max} (KBr disc) 2961(s), 2951 (s), 2932 (s), 2924 (s), 2869 (m), 2857(m), 1491(m), 1451(m), 1441(m), 1370(m), 1271(m), 1250(s), 1223(s), 1181 (m), 1150 (m), 1076 (m), 1065 (s), 1049 (s), 1026 (m), 1010 (m), 943 (m), 903 (m), 756 (m), 698 (m), 529 (m) cm^{-1} ; MS m/e 335 M^+ , 198, 138, 137, 105, 83, 69, 55, 41.

12. (+)-1-Phenylethylthiol (119)

A solution of (-)-O-menthyl-S-1-phenylethylthiocarbonate 4.3g (12.8 mmols) in toluene (25 ml) was refluxed with a large excess of morpholine (8.5g) for 4 hrs under N_2 . The reaction mixture was cooled, washed with water and dried over Na_2SO_4 and solvent evaporated off. The oily residue was dissolved in ethanol (40 ml) and the resulting solution was treated dropwise with a solution of $HgCl_2$ 3.6g (13.2 mmols) in ethanol (15 ml) while stirring. The white precipitate of (+)-1-phenylethylthiomercury chloride was collected by filtration and washed several times with ethanol. This crude material was added under N_2 to conc. HCl (30ml). The resulting suspension was then stirred until the solid had completely disappeared. The oily material was removed and dissolved in chloroform, washed with water and dried. After removal of the solvent the oil was distilled under reduced pressure to give the thiol as a colourless oil b.pt. $86-87^\circ C/17$ torr (0.8946g, 50.6%). Found: C, 69.35; H, 7.52%. $C_8H_{10}S$ requires C, 69.56; H, 7.25%; δ_H (200 MHz, $CDCl_3$) 7.38-7.17 (m, 5H, 5 x ArH), 4.20 (dq, $J=5Hz, 7Hz$, 1H, ArCH(CH_3)SH), 1.97 (d, $J=5Hz$, 1H, ArCH(CH_3)SH), 1.64 (d, $J=7Hz$, 3H, ArCH(CH_3)SH); δ_C (50 MHz, $CDCl_3$) 145.85 (s), 128.64(d), 127.14(d), 126.39(d), 38.72(d), 26.10(q); ν_{max} ($CHCl_3$ soln.) 3681 (w), 3673(w), 2870(m), 2570(w), 2434(m), 2402(s), 1948(w), 1877(w), 1804(w), 1752(w), 1603(s), 1584(m), 1561(w), 1522(s), 1377(s), 1341(w), 1300 (m), 1287(m), 1111(m), 1092(m), 1051(s), 1028(s), 1005(m), 972(m), 928(m), 910(m) cm^{-1} ; MS m/e 138 M^+ , 105, 91, 78, 63.

13. 1-(*p*-Methoxyphenyl)-3,4-dihydronaphthalene

To magnesium bromoanisole, prepared from magnesium, 6g (0.257 mols) and bromoanisole, 50g (0.267 mols) in dry diethyl ether (180 ml), was added, over 1½ hrs at 0°C, α -tetralone, (freshly distilled), 12g (0.16 mols) in dry ether (180 ml) and then refluxed for 30 mins. The complex was then hydrolysed with an iced solution of NH_4Cl . This finally gave the crude carbinol as a brown oil which was directly dehydrated by distillation (b.pt. 210-214°C). The product was then recrystalled from 120 ml of MeOH to give 23.55g (60-70%) of product. m.pt. 73-75°C; δ_{H} (200 MHz, CDCl_3) 7.29-6.88 (m, 8H, ArH), 6.04 (m, 1H, C=CH), 3.82 (s, 3H, ArOCH_3), 2.83 (m, 2H, ArCH_2), 2.36 (m, 2H, C=CCH₂); δ_{C} (50MHz, CDCl_3) 158.74 (s), 139.25 (s), 136.83(s), 135.24(s), 133.14(s), 129.76(d), 127.49 (d), 55.242(q), 28.29(t), 23.45 (t); ν_{max} (KBr disc) 3055 (w), 3025(m), 3015(m), 2940 (m), 2925(m), 2825(m), 1605(m), 1508(s), 1482(m), 1460(m), 1454(m), 1450(w), 1440(w), 1428(w), 1287(m), 1246(s), 1174(s), 1150(w), 1109(w), 1035(s), 960(w), 843(m), 820(s), 791(w), 778(w), 769(s), 746(m), 621(w), 608(m), 580(w), 549(w), 503(w) cm^{-1} ; MS m/e 236 M^+ , 214, 171, 128, 77, 28.

14. 1-(*p*-Methoxyphenyl)naphthalene

1-*p*-Methoxyphenyl-3,4-dihydronaphthalene, 1.18g (5 mmols) was added to 2,3-dichloro,5,6-dicyanoquinone (DDQ), 1.16g (5 mmols) in 5 ml of toluene and refluxed under nitrogen until all the red colour has disappeared (45 mins.). Then more DDQ, 1.10g (5 mmols) was added and refluxed for another 75 mins. The mixture was then diluted with 5 volumes of light petrol (40-60°C) and the ppt formed was filtered off. The solution was concentrated and then columned through an alumina column and was eluted with petrol (40-60°C) until no more product was obtained. The petrol was removed and the product recrystallised from MeOH (0.71g, 61%). m.pt. 114-115°C. δ_H (200 MHz, $CDCl_3$) 8.0 - 7.75 (m, 3H, ArH), 7.50-7.35 (m, 6H, ArH), 7.05-6.96 (m, 2H, ArH), 3.85(s, 3H, ArOCH₃); δ_C (50 MHz, $CDCl_3$) 158.9(s), 139.88(s), 133.81(s), 133.08(s), 131.80(s), 131.08(d), 128.23(d), 127.29(d), 126.87(d), 126.03(d), 125.88(d), 125.66(d), 125.37(d), 113.68(d), 55.28(q); ν_{max} (CHCl₃ sol.) 3061(m), 3047(m), 3011(m), 2958(w), 2936(w), 2911(w), 2838(m), 1610(s), 1593(w), 1574(w), 1515(s), 1506(s), 1464(m), 1442(m), 1412(w), 1396(w), 1286(s), 1246(s), 1176(s), 1118(w), 1109(w), 1036(s), 964(w), 840(s), 802(s), 582(m), 570(m), 431(w) cm⁻¹; MS m/e 234 M⁺ 219, 203, 189, 163, 117, 101, 94, 28.

15. *p*-(1-Naphthyl)phenol (120)

Methoxyphenyl-1-naphthalene, 5g (21.4 mmols) was dissolved in 50ml of CH_2Cl_2 under a nitrogen atmosphere at -78°C . BBr_3 , *ca.* 12ml (128.4 mmols) was then injected and the reaction allowed to rise slowly to r.t. and stirred for 12 hrs. Moist ether was then added, slowly, until no further reaction was detected. The precipitate was then filtered off and recrystallised from cyclohexane 4.7g (100%). m.pt. $138-140^\circ\text{C}$; δ_{H} (200 MHz, CHCl_3) 7.93-7.78 (m, 3H, ArH), 7.50-7.32 (m, 6H, ArH), 6.96-6.90 (m, 4H, ArH), 5.39 (s, 1H, ArOH); δ_{C} (50 MHz, CDCl_3) 154.73 (s), 139.81(s), 133.87(s), 133.48(s), 131.83(s), 131.41(d), 128.34(d), 127.45(d), 126.98(d), 126.05(d), 125.80(d), 125.48(d), 115.27(d). ν_{max} (CHCl_3 sol.) 3595 (m), 3412 (b,w), 3062 (w), 3012(m), 1612(s), 1594(w), 1328(w), 1200(s), 1172(s), 1101(w), 1020(w), 838(m), 802(s), 793(w), 769(s), 756(s), 745(m), 570(m), 557(w), 512(w), 434(w), 407(w) cm^{-1} ; MS m/e 222M^+ , 220, 203, 189, 165, 101, 94, 82.

GENERAL PROCEDURES

16. For Thiolate Synthesis

Method A: Sodium (48 mmols) was added directly to a 3-necked flask, equipped with a condenser and nitrogen flow, containing dry absolute alcohol (50 ml) and stirred. When the sodium had all reacted, indicating complete formation of ethoxide, the thiol (50 mmols) was added. The solution was stirred vigorously at room temperature for a further 20 mins, then evaporated to dryness, producing the crude thiolate salt. Purification of the salt was effected by washing on a sinter with sodium dried ether. The salt was quickly transferred to a round bottomed flask and dried at reduced pressure (oil pump). Having dried the salt, it was stored permanently under vacuum.

Method B: To a 3-necked 100 ml round bottomed flask, equipped with condenser and nitrogen bleed, was added the thiol (35 mmols) and dry degassed DMEU (35 mls). The nitrogen flow was then stopped and 95% sodium hydride (36 mmols) added. After all the hydrogen was evolved, the sample was put in a 50ml quick fit conical flask and degassed.

17. For Phenolate Synthesis

The phenol (13.5 mmols) was added directly to a 3-necked flask, equipped with a condenser and nitrogen flow, containing dry THF, and was allowed to dissolve. Then 95% sodium hydride (15 mmols) or sodium (15 mmols) was added and stirred vigorously at room temperature until no more hydrogen was evolved. The THF was then removed and the material pumped to dryness (oil pump) and stored under vacuum.

ANTHRACENE CORE UNIT

18. Decakis(cyclopentylthio)anthracene (127)

Method A, from perfluoroperhydroanthracene (125)

Perfluoroperhydroanthracene, 0.312g (0.5 mmol) and sodium cyclopentanethiolate, 3.10g (25 mmol), prepared from cyclopentanethiol and sodium according to the method of experiment 16 (Method A), were stirred in 30ml of degassed DMEU, under vacuum at 60°C for 7 days in the absence of light. The mixture was added to toluene (200 ml) and washed with water (10 x 100 ml). Evaporation of the solvent left a dark red oil from which (127) was obtained (as its 1,4-dioxane adduct) on recrystallisation from 1,4-dioxane/MeOH; yield 0.057g (9.7%); m.pt. 243-244°C. TLC, R_f = 0.31, diethyl ether/pet. ether (40-60°C) [1:30]; δ_H (200 MHz, $CDCl_3$), 4.32 (m, 4H, 4 x ArSCH), 4.05 (m, 4H, 4 x ArSCH), 3.09 (m, 2H, 2 x ArSCH), *ca.* 0.7-2.2 (m, 80H, 40 x CH_2); FAB MS m/e ($M + H$)⁺ 1179.

19. Decakis(cyclopentylthio)anthracene (127)

Method B, from fluorocarbon olefin mixture (126)

To a solution of sodium cyclopentylthiolate in DMEU (30ml), prepared from cyclopentylthiol 3.50g, (34 mmol) and sodium hydride (95%), 0.86g (35 mmols) according to the method of experiment 16 (Method B), was added the fluorocarbon olefin mixture (126) 0.415g (*ca.* 0.71 mmols). The reaction was then degassed and stirred, in the absence of light, for 20 hours. The resulting mixture was added to toluene (200 ml) and washed with water (10 x 100 ml). Evaporation of the solvent left a dark red oil from which (127) was obtained (as its 1,4-dioxane adduct) on recrystallisation from 1,4-dioxane/MeOH: yield 0.34g (*ca.* 37%), m.pt. 243-244°C. TLC R_f = 0.31, diethyl ether / pet.ether (40-60°C) [1:30]; Found: C, 63.74; H, 7.75; S, 24.00%, $C_{64}H_{90}S_{10}$: $1\frac{1}{2} C_4H_8O_2$ requires C, 64.07; H, 7.83; S, 24.44%; δ_H (200 MHz, $CDCl_3$) 4.32 (m, 4H, 4 x ArSCH), 4.05 (m, 4H, 4 x ArSCH), 3.09 (m, 2H, 2 x ArSCH), *ca.* 0.7-2.2 (m, 80H, 40 x CH_2); δ_C (50 MHz, $CDCl_3$) 143.39(s), 136.94(s), 132.70(s), 50.75(d) 48.43(d), 48.25(d), 33.51(t), 33.25(t), 32.90(t), 32.74(t), 32.17(t), 25.19(t), 25.17(t), 24.98(t), 24.74(t), 24.33(t); ν_{max} (KBr disc) 2960(s), 2860(m), 1630(b,m), 1445 (m), 1400 (m), 1380 (m), 1310(m), 1250 (m), 1120(m), 1080(w), 1065(m), 930(w), 900(w), 870(w), 830(w), 680(m), 620(w), 490(m) cm^{-1} ; FAB MS m/e ($M + H$)⁺ 1179.4330, ($C_{64}H_{90}S_{10}$ requires 1179.4328) 1109, 1077, 1044, 1009, 973, 940, 902, 870, 833, 802, 768, 734, 695, 665, 627, 597, 559, 529.

20. Decakis(cyclohexylthio)anthracene (128)

Sodium cyclohexylthiolate, prepared from cyclohexylthiol, 5g (43.1 mmols) and sodium hydride (95%), 1.15g (45.5 mmols) according to the method of experiment 16 (Method B), was reacted with the fluorocarbon olefin mixture **(126)** 0.574g (0.97 mmols) in DMEU (30ml), and worked-up according to the method of experiment 19. The red oil formed was purified by recrystallisation from diether ether to give purple crystals 0.1345g (10.417%) m.pt. 276-278°C. TLC R_f = 0.38, diethyl ether / pet.ether (40-60°C) [1:30]. Found: C, 67.48; H, 8.30%. C₇₄H₁₁₀S₁₀ requires C, 67.37; H, 8.34%. δ_{H} (200 MHz, CDCl₃, 330K) 3.92-3.82 (m, 4H, 4 x ArSCH), 3.53-3.48 (m, 4H, 4 x ArSCH) 2.50-2.35 (m, 2H, 2 x ArSCH), 2.11-0.68 (m, 100H, 50 x CH₂); δ_{C} (50 MHz, CDCl₃) 143.14(s), 137.66(s), 136.65(s), 131.22(s), 50.04(d), 48.99(d), 48.50(d), 33.32(t), 32.62(t), 32.54(t), 26.15(t), 25.96(t), 25.88(t), 25.74(t), 25.52(t); ν_{max} (KBr disc) 2926(s), 2851(m), 1630(bm), 1445(m), 1382(m), 1338(w), 1306(w), 1260(m), 1212(w), 1136(w), 1067(w), 996(w), 681(w), 486(w) cm⁻¹.

21. Decakis(cycloheptylthio)anthracene (129)

Sodium cycloheptylthiolate was made from cycloheptylthiol, 3.24g (25 mmols) and sodium hydride (95%), 0.63g (25 mmols) according to the method of experiment 16 (Method B). It was then reacted with the fluorocarbon olefin mixture (128) 0.332g (*ca.* 0.57 mmols) in DMEU (30 ml), and worked-up according to the method of experiment 19. The red oil was purified from 1,4-dioxane/MeOH to give purple crystals. 0.1092g (13.22%) m.pt. 255°C. TLC $R_f = 0.33$, diethylether / pet. ether (40-60°C) [1:20]; Found: C, 68.94; H, 8.85% $C_{84}H_{130}S_{10}$ requires C, 69.13; H, 8.91%; δ_H (200 MHz, $CDCl_3$) 4.25 (m, 4H, 4 x ArSCH), 3.98 (m, 4H, 4 x ArSCH), 3.01 (m, 2H, 2 x ArSCH), *ca.* 2.09-0.68 (m, 120H, 60 x CH_2); δ_C (50 MHz, $CDCl_3$), 143.36(s), 136.89(s), 132.66(s), 50.70(d), 48.38(d), 48.21(d), 33.46(t), 33.20(t), 32.86(t), 32.69(t), 32.13(t), 25.15(t), 25.11(t), 24.93(t), 24.69(t), 24.29(t); ν_{max} (KBr disc) 2924(s), 2851(s), 1456(m), 1449(m), 1443(m), 1344(w), 1279(w), 1252(w), 1225(w), 1204(w), 953 (w), 831.43(w) cm^{-1} .

22. Decakis(*S*-camphorthio)anthracene (130)

Sodium (*S*)-camphorthiolate in DMEU (30ml) was made from (*S*)-10-mercaptocamphor, 5g (27.2 mmols) and sodium hydride (95%), 0.70g (27.7 mmols) according to the method of experiment 16 (Method B). It was then reacted overnight with the fluorocarbon olefin mixture (126), 0.362g (*ca.* 0.62 mmols) and worked up according to the method of experiment 19. The red oil was then purified by preparative plate chromatography, toluene:diethyl ether [1:1] to yield a purple solid, 0.2954g (23.9%); m.pt. 194-197°C. TLC R_f = 0.33, toluene/diethyl ether [1:1]; δ_H (200 MHz, $CDCl_3$) 3.85-3.70(m, 2H), 3.45-3.20 (m, 5H), 3.15-3.05 (m, 2H), 3.00-2.78 (m, 5H), *ca.* 2.50-1.50 (m, *ca.* 66H), *ca.* 1.50-0.50 (m, *ca.* 70H); δ_C (50 MHz, $CDCl_3$) 217.07 (s), 216.54(s), 216.12(s), 148.06(s), 145.66(s), 140.46(s), 140.21(s), 138.46(s), 138.48(s), 127.15(s), 135.64(s), 66.47(t), 61.56(s), 61.49(s), 61.16(s), 60.99(s), 55.10(t), 48.20(s), 47.97(s), 47.90(s), 47.81(s), 47.63(s), 43.65(d), 43.46(d), 43.28(d), 43.10(t), 43.00(t), 42.83(t), 37.18(t), 36.13(t), 35.90(t), 35.16(t), 33.18(t), 29.70(t), 27.06(t), 26.69(t), 26.59(t), 26.15(t), 26.03(t), 25.65(t), 20.94(q), 20.48(q), 20.35(q), 20.27(q), 20.23(q), 20.18(q), 20.05(q), 19.87(q); ν_{max} ($CHCl_3$ soln.) 3015 (s), 2965(s), 2930(m), 1737(s), 1450(m), 1414(m), 1390(m), 1373(m), 1222(s), 1216(s), 1210(s), 1198(m), 1050(m), 930(m), 668(s) cm^{-1} .

23. Attempted formation of decakis(phenylthio)anthracene

Sodium phenylthiolate 1.5g (11.4 mmols), made according to the method of experiment 16 (Method A) from thiophenol and sodium, was added to DMPU (30ml) and degassed. The reaction was cooled to -10°C and the fluorocarbon olefin mixture (126), 0.133g (0.23 mmols) added. The reaction was then stirred at -10°C , in the absence of light for 3 hours and left to warm to room temperature overnight and then worked-up according to the method of experiment 19. The red oil was partially purified by a gravity column toluene/pet. ether ($40-60^{\circ}\text{C}$) but on reverse plate TLC there were 4 spots (1 purple) none of which could be isolated. No further analysis was carried out.

24. Attempted formation of decakis(*m*-tolylthio)anthracene

Sodium *m*-tolylthiolate in DMEU (30ml) was prepared from *m*-tolylthiol (95%), 2.7g (21 mmols) and sodium hydride (95%), 0.55g (23 mmols) according to the method of experiment 16 (Method B). It was then reacted overnight with the fluorocarbon olefin mixture (126), 0.242g (*ca.* 0.41 mmols) and worked-up according to the method of experiment 19. The red oil left contained 3 main spots purple (*R_f* = 0.33), orange (*R_f* = 0.45) and yellow (*R_f* = 0.53) which could not all be separated by column, however, an orange oil was obtained, 30 mg (6.3%); TLC *R_f* = 0.45, Toluene/pet. ether (40-60°C) [1:1]; δ_{H} (200 MHz, CDCl₃). 10.14 (s, 2H, 9,10 AnthH), 6.99-6.73 (m, 32H, 32 x ArH), 2.16 (s, 12H, 4 x ArCH₃), 2.08 (s, 12H, 4 x ArCH₃).

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25. Dodecafluorotriphenylene (132)

To a flame dried tube was added 1,2-diiodotetrafluorobenzene 5g (12.5 mmols) and copper bronze 10g, (157 mmols). The tube was sealed under vacuum (oil pump) and heated for 200°C for 18 hrs. The mixture was then extracted with dichloromethane and filtered, purified by gravity column eluted with pet. ether (40-60°C) to give a white crystalline solid, 0.46g (25%) m.pt. 109-110°C; Found: C, 48.64; F, 51.68%. $C_{18}F_{12}$ requires C, 48.65; F, 51.35%; MS m/e M^+ 443.9786 ($C_{18}F_{12}$ requires 444.1740), 413, 375, 344, 313, 275, 222.

26. Dodecakis(phenoxy)triphenylene (134)

Sodium phenolate 1g, (8.62 mmols), prepared from phenol and sodium according to the method of experiment 17, was dissolved in DMEU (30ml) and the solution degassed. Perfluorotriphenylene 0.15g (0.34 mmols) was then added and the mixture degassed again and stirred at 90°C for 1 month. The resulting product was added to toluene (200 ml) and washed with water (10 x 100ml). The toluene was then removed and the oil purified by gravity column, diethyl ether/pet. ether (40-60°C) [1:1]. The resulting off-white solid was recrystallised from chloroform/methanol to give clear crystals 0.1511g (33.6%); m.pt. 236-237°C. TLC R_f = 0.42 diethyl ether/pet.ether (40-60°C) [1:1]; Found: C, 81.16; H, 4.35%. $C_{90}H_{60}O_{12}$ requires C, 81.08; H, 4.50%; δ_H (200 MHz, $CDCl_3$) 7.16-6.89 (m, 36H, 36 x ArH), 6.42-5.28 (m, 24H, 24 x ArH); δ_C (50 MHz, $CDCl_3$) 158.11 (s), 157.60(s), 143.30(s), 142.70(s), 129.61(d), 129.48(d), 122.73(d), 122.61(d), 121.59(s), 115.83(d), 115.80(d); ν_{max} (KBr disc) 3063(w), 3040(w), 1591(s), 1572(w), 1561(w), 1489(s), 1466(m), 1456(m), 1412(s), 1364(w), 1337(m), 1210(s), 1165(m), 1074(m), 1065(m), 1022(w), 965(m), 845(w), 748(m), 687(m) cm^{-1} ; FAB MS m/e ($M + H$)⁺ 1333.411600, ($C_{90}H_{61}O_{12}$ requires 1333.416303).

27. Dodecakis(*m*-methylphenoxy)triphenylene (135)

Sodium *m*-methylphenolate, in DMEU (30ml), was prepared from *m*-methylphenol 1.2g (11.1 mmols) and sodium hydride (95%), according to the method of experiment 16 (Method B). It was reacted with perfluorotriphenylene, 0.164g (0.37 mmols) at 90°C for 1 month and worked up according to the method of experiment 26. The pale yellow oil was purified by gravity column diethylether/pet. ether (40-60°C) to give a pale yellow powder 0.091g (16.4%) m.pt. 61-65°C. TLC R_f = 0.42 diethylether/pet. ether (40-60°) [1:9]. Reverse phase TLC (methanol) shows two spots; Found C, 81.52; H, 5.51%, C₁₀₂H₈₄O₁₂ required C, 81.60; H, 5.60% ; δ_H (200 MHz, CDCl₃) 7.06-6.63 (m, 24H, 24 x ArH) 6.40-6.06 (m, 24H, 24 x ArH), 2.19-2.09 (2 x s, 36H, 12 x ArCH₃); δ_C (50 MHz, CDCl₃) 158.01(s), 157.24(s), 142.73(s), 142.17(s), 138.84(s), 138.62(s), 128.47(d), 128.41(d), 122.75(d), 122.60(d), 121.27(s), 117.03(d), 116.33(d), 112.53(d), 112.39(d), 112.04(d), 21.37(q), 21.19(q); ν_{max} (KBr disc) 3033(w), 2919(w), 1612(m), 1587(m), 1559(w), 1487(s), 1459(m), 1414(s), 1377(m), 1335(w), 1306(w), 1282(w), 1247(s), 1151(s), 1040(w), 1000(w), 971(w), 931(w), 772(m), 685(m) cm⁻¹.

28. Dodecakis(*p*-methylphenoxy)triphenylene (136)

Sodium *p*-methylphenolate 1.094g (8.42 mmols), prepared from *p*-methylphenol and sodium hydride 95% according to the method of experiment 17, was reacted with perfluorotriphenylene 0.15g (0.34 mmols) in DMEU (30 ml), at 90°C, for 1 month and worked up according to the method of experiment 26. The pale yellow oil was purified by gravity column, diethyl ether/pet. ether (40-60°C) [3:7] and the resulting off-white solid was recrystallised from dichloromethane/pet. ether (40-60°C) to give clear crystals 0.2294g (45.3%); m.pt. 211-212°C. TLC R_f = 0.41 diethyl ether / pet. ether (40-60°C) [3:7]; Found: C, 81.71; H, 5.82% $C_{102}H_{84}O_{12}$ requires C, 81.60; H, 5.60%; δ_H (200 MHz, $CDCl_3$) 6.81 (AA'BB', 24H, 24 x ArH), 6.25 (AA'BB', 24H, 24 x ArH), 2.28 (s, 18H, 6 x ArCH₃), 2.21 (s, 18H, 6 x ArCH₃); δ_C (50 MHz, $CDCl_3$) 155.99 (s), 155.40(s), 143.14(s), 142.43(s), 131.10(s), 131.03(s), 129.40(d), 129.24(d), 121.22(s), 115.52(d), 115.36(d), 20.65(q), 20.59(q); ν_{max} (KBr disc) 3569 (w), 3441 (w), 3029(w), 2922(w), 2863(w), 1609(m), 1591(w), 1561(w), 1505(s), 1460(m), 1414(s), 1364(w), 1335(m), 1285(w), 1215(s), 1167(s), 1113(w), 1105(w), 1065(m), 1015(w), 966(w), 853(w), 812(m), 500 (w) cm^{-1} .

29. Dodecakis(3,5-dimethylphenoxy)triphenylene (137)

Sodium 3,5-dimethylphenolate 1.46g (10.1 mmols), prepared from 3,5-dimethylphenol and sodium according to the method of experiment 17, was reacted with perfluorotriphenylene 0.133g (0.30 mmols) in DMEU (30 ml), at 90°C, for 1 month and worked up according to the method of experiment 26. The yellow oil was purified by gravity column, diethyl ether/pet. ether (40-60°C) [1:9] to yield a pale yellow solid 0.166g (50.0%); m.pt. 94-97°C TLC $R_f = 0.49$ diethyl ether / pet. ether (40-60°C) [3:7]. Reverse phase TLC (methanol) shows more than one spot. Found: C, 81.94; H, 6.35%, $C_{114}H_{108}O_{12}$ requires C, 82.01; H, 6.47% ; δ_H (200 MHz, $CDCl_3$) 6.54-5.70 (m, 36H, 36 x ArH), 2.11-2.03 (3 x s, 72H, 24 x $ArCH_3$); δ_C (50 MHz, $CDCl_3$) 158.22(s), 157.28(s), 157.18(s), 142.98(s), 142.72(s), 142.51(s), 142.37(s), 142.24(s), 138.72(s), 138.31(s), 138.19(s), 138.13(s), 138.08(s), 138.04(s), 137.98(s), 137.94(s), 137.89(s), 124.05(d), 123.94(d), 123.77(d), 123.65(d), 123.17(d), 123.06(d), 122.96(d), 121.67(s), 121.38(s), 121.27(s), 113.99(d), 113.73(d), 113.60(d), 113.41(d), 113.26(d), 21.16(q); ν_{max} (KBr disc) 3017(m), 2950(m), 2919(m), 2861(w), 1618(s), 1595(s), 1572(m), 1561(m), 1541(w), 1509(w), 1503(w), 1466(s), 1458(s), 1414(s), 1375(m), 1335(m), 1312(m), 1292(s), 1146(s), 1080(s), 1035(w), 833(s), 681(m) cm^{-1} .

30. Dodecakis(*p*-*t*-butylphenoxy)triphenylene (138)

Sodium *p*-*t*-butylphenolate 1.74g (10.1 mmols), prepared from *p*-*t*-butyl phenol and sodium hydride (95%) according to the method of experiment 17, was reacted with perfluorotriphenylene, 0.15g (0.34 mmols) in DMEU (30 ml), at 90°C, for 1 month and worked up according to the method of experiment 26. The pale yellow oil was purified by gravity column, diethyl ether/pet. ether (40-60°C) [1:9] to yield off-white crystals which were recrystallised from diethyl ether/hexane to yield clear crystals 0.151g (22.3%) m.pt. 160-164°C. TLC R_f = 0.47 diethyl ether/Pet. ether (40-60°) [1:9]; Found: C, 81.41; H, 7.95%, C₁₃₈H₁₅₆O₁₂ requires C, 82.63; H, 7.78%; δ_H (200 MHz, CDCl₃,) 7.07-6.95 (m, 24H, 24 x ArH), 6.39-6.23 (m, 24H, 24 x ArH), 1.26-1.22 (2 x s, 108H, C(CH₃)₃); δ_C (50 MHz, CDCl₃,) 155.85(s), 155.04(s), 144.42(s), 144.20(s), 143.04(s), 142.13(s), 125.50(d), 121.28(s), 115.25(d), 34.01(s), 31.54(q), 31.49(q); ν_{max} (KBr disc) 2963(s), 2904(w), 2868(w), 1608(w), 1508(s), 1462(m), 1417(s), 1363(m), 1335(w), 1291(w), 1267(m), 1223(s), 1175(s), 1111(w), 1065(m), 1013(w), 967(w), 827(m), 545(w) cm⁻¹.

31. Dodecakis(*p*-cumylphenoxy)triphenylene (139)

Sodium *p*-cumylphenolate, 2.37g (10.1 mmols), prepared from *p*-cumyl phenol and sodium hydride (95%) according to the method of experiment 17, was reacted with perfluorotriphenylene 0.15g (0.34 mmols) in DMEU (30 ml), at 90°C, for 1 month and worked up according to the method of experiment 26. The yellow oil is purified by gravity column, toluene/pet. ether (40-60°C) [7:3] to yield a pale yellow solid 0.433g (46.6%); m.pt. 90-93°C. TLC R_f = 0.57 toluene/pet. ether (40-60°C) [7:3]; Found: C, 86.43; H, 6.58% $C_{198}H_{180}O_{12}$ requires C, 86.46; H, 6.55%; δ_H (200 MHz, $CDCl_3$) 7.20-6.98 (m, 60H, 60 x *ArH*), 6.70 (AA'BB', 24H, 24 x *ArH*), 6.27 (AA'BB', 12H, 12 x *ArH*), 6.10(AA'BB', 12H, 12 x *ArH*), 1.58 - 1.44 (2 x s, 72H, 12 x $ArC(CH_3)_2Ar$); δ_C (50 MHz, $CDCl_3$) 155.54(s), 155.11(s), 150.81(s), 144.27(s), 144.05(s), 142.7(s), 141.39(s), 127.98(d), 127.93(d), 127.31(d), 126.67(d), 126.58(d), 125.56(d), 125.43(d), 120.72(s), 115.16(d), 42.33(s), 42.22(s), 30.89(q); ν_{max} (KBr disc) 3087 (m), 3058(m), 2969(m), 2934(m), 2872(m), 1503(s), 1474(w), 1466(w), 1458(w), 1445(w), 1420(m), 1383(w), 1364(w), 1219(s), 1173(m), 1065(w), 828(w), 764(w), 700(m) cm^{-1} .

32. Dodecakis(*p*-naphthyl phenoxy)triphenylene (140)

Sodium *p*-naphthylphenolate 2.45g (10.1 mmols), prepared from *p*-naphthylphenol and sodium hydride (95%) according to the method of experiment 17, was reacted with perfluorotriphenylene, 0.145g (0.33 mmols) in DMEU (30 ml), at 90°C, for 1 month and worked up according to the method of experiment 26. The pale yellow oil was purified by gravity column, toluene/pet. ether (40-60°C) [7:3] to yield a pale yellow powder 0.373g (40.2%) m.pt. 142-145°C. TLC R_f = 0.57 toluene/pet. ether (40-60°C) [7:3]; Found: C, 88.53; H, 4.42% $C_{210}H_{132}O_{12}$ requires C, 88.61; H, 4.64%; δ_H (200 MHz, $CDCl_3$) 7.97-7.73 (m, 36H, 36 x *ArH*), 7.48-7.01 (m, 96H, 96 x *ArH*); δ_C (50 MHz, $CDCl_3$) 157.50(s), 156.68(s), 143.49(s), 142.69(s), 139.50(s), 139.16(s), 135.23(s), 135.10(s), 133.82(s), 133.77(s), 131.65(s), 131.53(s), 131.00(d), 130.89(d), 128.24(d), 127.5(d), 127.05(d), 126.91(d), 126.11(d), 125.73(d), 125.67(d), 125.36(d), 125.28(d), 121.78(s), 115.95(d); ν_{max} (KBr disc) 3040(m), 1510(s), 1501(s), 1460(m), 1414(s), 1395(s), 1331(w), 1211(s), 1167(s), 1067(w), 963(w), 835(w), 799(s), 791(m), 775(s), 567(w) cm^{-1} .

33. Dodecakis(*p*-phenylphenoxy)triphenylene

Sodium *p*-phenylphenolate, 1.95g (10.1 mmols), prepared from *p*-phenyl phenol and sodium according to the method of experiment 17, was reacted with perfluorotriphenylene 0.145g (0.33 mmols) in DMEU (30 ml), at 90°C, for 1 month and worked up according to the method of experiment 26. The yellow oil was purified by gravity column toluene/pet. ether (40-60°C) [7:3] to yield an off white solid which recrystallised from 1,4-dioxane/*i*-propyl alcohol to yield clear crystals 0.4239g (55.9%) m.pt. 173-175°C. TLC R_f = 0.45 toluene/pet. ether (40-60°C) [7:3]; Found: C, 86.74; H, 4.85% $C_{162}H_{108}O_{12}$ requires C, 86.63; H, 4.81%; δ_H (200 MHz, CD_2Cl_2) 7.46-7.39 (m, 24H, 24 x ArH), 7.30-7.23 (m, 48H, 48 x ArH), 7.11 (d, $J=8.8$ Hz, 12H, 12 x ArH), 6.65 (d, $J=8.8$ Hz, 12H, 12 x ArH), 6.46 (d, $J=8.8$ Hz, 12H, 12 x ArH); δ_C (50 MHz, $CDCl_3$) 157.34(s), 156.75(s), 142.71(s), 142.55(s), 140.24(s), 139.95(s), 135.26(s), 135.19(s), 128.87(d), 128.58(d), 127.70(d), 127.58(d), 126.99(d), 126.64(d), 121.06(s), 116.03(d), 115.93(d); ν_{max} (KBr disc) 3056(m), 3028(m), 1606(m), 1512(s), 1484(s), 1458(w), 1450(m), 1412(s), 1332(w), 1266(w), 1216(s), 1184(m), 1168(s), 1066(m), 1006(w), 832(m), 760(s), 696(m) cm^{-1} ; FAB MS m/e (M+H)⁺ 2246, 2078, 1908, 1739, 1585, 1417.

34. Attempted formation of Dodecakis(*o*-methylphenoxy)triphenylene

Sodium *o*-methylphenolate 1.44g (11.1 mmols), prepared from *o*-methylphenol and sodium hydride (95%) according to the method of experiment 17, was reacted with perfluorotriphenylene, 0.15g (0.34 mmols) in DMEU (30 ml), at 90°C, for 2 months and worked up according to the method of experiment 26. The yellow oil showed many spots on the TLC. Diethyl ether/pet. ether (40-60°C), none of which could be isolated. No further analysis was carried out.

35. Attempted formation of dodecakis((S)-(-)-1-methyl-2-pyrrolidine methoxy)triphenylene

Sodium (S)-(-)-1-methyl-2-pyrrolidine methoxide in HMPA (30 ml, prepared from (S)-(-)-1-methyl-2-pyrrolidine methanol 1.17g (10.2 mmols) and sodium hydride (95%) 0.2676g (10.6 mmols) according to the method of experiment 16 (Method B), was reacted with perfluorotriphenylene 0.15g (0.34 mmols) for 1 month and worked up according to the method of experiment 26. The brown oil showed many spots on TLC methanol/ammonia [15:1] none of which could be isolated. No further analysis was carried out.

36. Dodecakis(phenylthio)triphenylene (142)

Sodium thiophenolate 1.1g (8.33 mmols), prepared from thiophenol and sodium according to the method of experiment 16 (Method A), was dissolved in DMEU (30 ml) and the solution degassed. Perfluorotriphenylene 0.123g (0.28 mmols) was then added and the mixture is degassed again and stirred, at 60°C, for 5 days. Toluene (200 ml) was then added and the organic layer washed with water (10 x 100 ml). After the solvent was removed the red oil was purified by a gravity column, toluene /pet. ether (40-60°C) [6:4] to yield a red powder 0.27g (64%) m.pt. 108-110°C. TLC R_f = 0.23 toluene/pet. ether (40-60°C) [6:4]; Found: C, 70.84; H, 3.72; S, 25.22% C₉₀H₆₀S₁₂ requires C, 70.87; H, 3.94; S, 25.19%; δ_H (200 MHz, CD₂Cl₂) 7.20-6.74 (m, *ca.* 44H, 44 x ArH), *ca.* 6.60-6.30(m, *ca.* 16H, 16 x ArH); δ_C (50 MHz, CD₂Cl₂) 144.50(s), 144.39(s), 144.33(s), 139.81(s), 139.19(s), 138.94(s), 138.77(s), 138.48(s), 138.13(s), 137.79(s), 136.98(s), 135.87(s), 129.44(d), 129.37(d), 129.33(d), 129.25(d), 129.04(d), 128.85(d), 128.58(d), 128.37(d), 127.83(d), 126.98(d), 126.80(d), 126.70(d), 126.34(d), 126.08(d); ν_{max} (KBr disc) 3052(s), 1580(s), 1478(s), 1439(s), 1256(m), 1080(w), 1067(w), 1024(m), 735(s), 698(m), 687(s) cm⁻¹.

37. Octakis(phenylthio)tetrafluorotriphenylene (143)

Sodium thiophenolate 0.743g (5.63 mmols), prepared from thiophenol and sodium according to the method of experiment 16 (Method A), was reacted with perfluorotriphenylene 0.1g (0.23 mmols), in DMEU (30 ml) and the solution degassed. It was then stirred at room temperature for three and half hours, and worked up according to the method of experiment 36. The resulting red oil was purified by crystallisation from diethyl ether/chloroform/methanol to yield brown red crystals 84 mg (13%). m.pt. 166-167°C. TLC R_f = 0.40 toluene/pet. ether (40-60°C) [6:4]; δ_H (200 MHz, $CDCl_3$) *ca.* 7.35-7.15 (m, 26H, 26 x *ArH*), *ca.* 7.10-7.03 (m, 4H, 4 x *ArH*), *ca.* 6.95-6.85 (m, 2H, 2 x *ArH*), 6.80-6.70 (m, 4H, 4 x *ArH*), 6.53-6.49 (m, 4H, 4 x *ArH*); δ_C (50 MHz, $CDCl_3$) 158.75(s), 157.89(s), 156.56(s), 152.84(s), 151.96(s), 151.47(s), 142.94(s), 141.32(s), 137.16(s), 136.83(s), 135.88(s), 135.29(s), 134.66(s), 134.62(s), 132.18(s), 132.09(s), 131.18(d), 129.95(d), 129.47(d), 129.36(d), 129.15(d), 129.04(d), 128.78(d), 128.29(d), 128.05(d), 127.26(d), 127.00(d), 126.63(d), 126.36(d), 122.29(s), 122.00(s), 115.47(s); δ_F (188MHz, $CDCl_3$) -89.96 (t, $J=7.14\text{Hz}$), -96.78 (t, $J=7.33\text{Hz}$); ν_{max} (KBr disc) 3054(m), 1580(s), 1561(m), 1478(s), 1439(s), 1416(m), 1381(m), 1329(m), 1258(m), 1213(w), 1175(w), 1156(w), 1121(w), 1080(m), 1069(m), 1024(m), 999(w), 959(w), 897(w), 889(w), 860(m), 793(w), 735(s), 700(w), 687(s), 669(w), 619(w), 558(w), 735(s), 700(w), 687(s), 669(w), 619(w), 558(w), 486(w), 434(w) cm^{-1} ; FAB MS m/e (M^+) 1164.

38. Dodecakis(*p*-tolylthio)triphenylene (144)

Sodium *p*-tolylthiolate 1.48g (10.1 mmols), prepared from *p*-tolylthiol and sodium according to the method of experiment 16 (Method A), was reacted with perfluorotriphenylene, 0.15g (0.34 mmols) in DMEU (30 ml), at 60°C, for 2 weeks and worked up according to the method of experiment 36. The orange oil was purified by gravity column, diethyl ether/pet. ether (40-60°C) [2:8] and recrystallised from ether to give orange crystals 0.459g (80%). m.pt. 221-222°C TLC R_f = 0.16 diethyl ether/pet. ether (40-60°C) [2:8]; Found: C, 72.13; H, 4.85; S, 22.48% C₁₀₂H₈₄S₁₂ requires C, 72.34; H, 4.96; S, 22.69%; δ_H (200 MHz, CDCl₃) *ca.* 6.89-6.29 (m, 48H, 48 x ArH), 2.32 (s, 6H, 2 x ArCH₃), 2.27 (s, 6H, 2 x ArCH₃), 2.22 (s, 6H, 2 x ArCH₃), 2.13 (s, 6H, 2 x ArCH₃), 2.07 (s, 6H, 2 x ArCH₃), 2.05 (s, 6H, 2 x ArCH₃); δ_C (50 MHz, CDCl₃) 148.54(s), 144.02(s), 139.25(s), 137.96(s), 137.46(s), 136.63(s), 135.82(s), 135.65(s), 135.39(s), 135.22(s), 135.16(s), 135.03(s), 134.89(s), 134.43(s), 134.36(s), 133.21(s), 129.55(d), 129.41(d), 129.23(d), 129.14(d), 128.87(d), 128.55(d), 128.31(d), 127.62(d), 21.14(q), 20.99(q), 20.84(q); ν_{max} (KBr disc) 3016(w), 2916(m), 2860(w), 1490(s), 1456(m), 1452(m), 1396(w), 1376(w), 1254(m), 1210(w), 1180(w), 1116(w), 1084(m), 1016(m), 800(s), 756(w), 486(m) cm⁻¹; FAB MS m/e (M+H)⁺ 1693, 1571, 1447, 1355, 1325, 1233.

39. Dodecakis(*p-t*-butyl phenylthio)triphenylene (145)

Sodium *p-t*-butylphenylthiolate 1.72g (9.15 mmols), prepared from *p-t*-butylthiophenol and sodium according to the method of experiment 16 (Method A), was reacted with perfluorotriphenylene, 0.15g (0.36 mmols) in DMEU (30 ml), at 60°C, for 1 week and worked up according to the method of experiment 36. The orange oil was purified by gravity column, diethyl ether/pet. ether (40-60°C) [1:20]; Found: C, 75.24; H, 7.12; S, 17.24%. $C_{138}H_{156}S_{12}$ requires C, 75.41; H, 7.10; S, 17.49%; δ_H (200 MHz, $CDCl_3$) *ca.* 7.19-6.50 (m, 48H, 48 x ArH), 1.29 (s, 18H, 2 x $C(CH_3)_3$), 1.21 (s, 18H, 2 x $C(CH_3)_3$), 1.20 (s, 18H, 2 x $C(CH_3)_3$), 1.10 (s, 36H, 4 x $C(CH_3)_3$), 0.98 (s, 18H, 2 x $C(CH_3)_3$); δ_C (50 MHz, $CDCl_3$) 149.43(s), 148.86(s), 148.82(s), 148.62(s), 148.55(s), 147.89(s), 145.26(s), 143.38(s), 142.53(s), 140.28(s), 138.64(s), 137.92(s), 137.17(s), 136.78(s), 136.11(s), 135.99(s), 134.75(s), 134.67(s), 133.86(s), 128.89(d), 128.79(d), 128.58(d), 128.02(d), 127.52(d), 125.72, 125.55(d), 125.32(d), 125.18(d), 34.48(s), 34.35(s), 34.20(s), 34.11(s), 31.38(q), 31.27(q), 31.23(q); ν_{max} (KBr disc) 2960(S), 2902(m), 2866(m), 1496(s), 1486(m), 1460(m), 1396(m), 1362(m), 1266(m), 1116(m), 1012(m), 818(s), 546(m) cm^{-1} ; FAB MS m/e (M+H)⁺ 2197, 2033, 1870, 1736, 1703, 1570.

40. Dodecakis(3,5-dimethylphenylthio)triphenylene (146)

Sodium 3,5-dimethylphenylthiolate 1.35g (8.44 mmols), prepared from 3,5-dimethylthiophenol and sodium according to the method of experiment 16 (Method A), was reacted with perfluorotriphenylene, 0.15g (0.34 mmols) in DMEU (30 ml), at 60°C, for 2 weeks and worked up according to the method of experiment 36. The orange oil was purified by gravity column, diethyl ether/pet. ether (40-60°C) [1:9] and recrystallised from diethyl ether/pet. ether (40-60°C) to give orange crystals 172 mg (27.4%) m.pt. 252-253°C. TLC R_f = 0.32 diethyl ether/pet. ether (40-60°C) [2:8]; Found: C, 73.44; H, 5.99; S, 20.85%. C₁₁₄H₁₀₈S₁₂ requires C, 73.54; H, 5.81; S, 20.64%; δ_H (200 MHz, CDCl₃) 6.74-5.99 (m, 36H, 36 x ArH), 2.03-1.67 (3 x s, 72H, 24 x ArCH₃); δ_C (500 MHz, CDCl₃) 148.70(s), 144.52(s), 143.73(s), 143.57(s), 139.01(s), 138.82(s), 138.16(s), 138.09(s), 137.98(s), 137.88(s), 137.84(s), 137.66(s), 137.45(s), 137.30(s), 137.19(s), 136.99(s), 136.77(s), 135.57(s), 129.00(d), 128.24(d), 128.11(d), 127.52(d), 126.84(d), 126.05(d), 125.86(d), 124.17(d), 21.18(q), 20.93(q), 20.86(q), 20.64(q); ν_{max} (KBr disc) 2946 (m), 2914(m), 2857(m), 1600(s), 1578(s), 1457(m), 1376(w), 1251(m), 1036(w), 837(s), 681(s) cm⁻¹.

41. Attempted formation of dodecakis(cyclopentylthio)triphenylene

Sodium cyclopentylthiolate 1.05g (8.45 mmols), prepared from cyclopentylmercaptan and sodium according to the method of experiment 16 (Method A), was reacted with perfluorotriphenylene 0.15g (0.34 mmols) in DMEU (30 ml), at 60°C, for 1 week and worked up according to the method of experiment 36. The orange oil showed many spots on the TLC, diethyl ether/pet. ether (40-60°C) [1:20], none of which could be isolated. No further analysis was carried out.

42. Attempted formation of dodecakis(cyclohexylthio)triphenylene

Sodium cyclohexylthiolate 1.17g (8.45 mmols), prepared from cyclohexyl mercaptan and sodium according to the method of experiment 16 (Method A), was reacted with perfluorotriphenylene 0.15g (0.34 mmols) in DMEU (30 ml), at 60°C, for 1 week and worked up according to the method of experiment 36. The orange oil showed many spots on the TLC, diethyl ether/pet. ether (40-60°C) [1:20], none of which could be isolated. No further analysis was carried out.

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43. Decakis(phenylthio)biphenyl (147)

Sodium phenylthiolate 1.86g (14.1 mmols), prepared from thiophenol and sodium according to the method of experiment 16 (Method A), was reacted with decafluorobiphenyl 0.235g (0.7 mmols) in DMEU (30 ml), at 60°C for 5 days and worked up according to the method of experiment 43. The pale yellow oil was purified by gravity column pet ether (40-60°C) /diethyl ether [6:4] to give a yellow foam 0.268g (30.9%). TLC R_f = 0.27 pet. ether (40-60°C)/diethyl ether [6:4]; δ_H (200 MHz, $CDCl_3$) 7.20-6.84 (m, 50H, 50 x ArH); δ_C (50 MHz, $CDCl_3$) 150.92(s), 149.00(s), 147.18(s), 141.19(s), 138.11(s), 137.45(s), 137.19(s), 128.74(d), 128.60(d), 128.20(d), 127.80(d), 126.98(d), 125.88(d), 125.77(d); ν_{max} (KBr disc) 3070(w), 3055(w), 1581(s), 1478(s), 1439(s), 1420(w), 1384(w), 1281(m), 1180(w), 1082(m), 1068(m), 1024(s), 999(w), 734(s), 698(s), 686(s). cm^{-1} ; FAB MS m/e (M^+) 1234, 1127, 1017, 939, 907.

44. Decakis(*p*-methylphenylthio)biphenyl (148)

Sodium *p*-methoxyphenylthiolate 1.75g (12 mmols), prepared from *p*-methylthiophenol and sodium according to the method of experiment 16 (Method A), was reacted with decafluorobiphenyl 0.200g (0.6 mmols) in DMEU (30 ml), at 60°C, for 10 days and worked up according to the method of experiment 43. The yellow oil was purified by gravity column, pet. ether (40-60°C)/diethyl ether [8:2] to yield yellow crystals 0.545g (66.2%) m.pt. 199-200 °C. TLC R_f = 0.30 pet. ether (40-60°C)/diethyl ether [8:2]; δ_H (200 MHz, $CDCl_3$) 6.91-6.62 (m, 40H, 40 x ArH), 2.24-2.22(2 x s, 18H, 6 x ArCH₃), 2.11 (s, 12H, 4 x ArCH₃); δ_C (50 MHz, $CDCl_3$) 150.04(s), 148.70(s), 146.55(s), 140.87(s), 135.28(s), 135.23(s), 135.16(s), 134.73(s), 134.08(s), 133.93(s), 129.36(d), 129.22(d), 128.27(d), 128.19(d), 127.31(d), 21.08(q), 21.04(q), 20.95(q); ν_{max} (KBr disc) 3016(w), 2973(w), 2917(m), 2862(w), 1490(s), 1448(w), 1281(m), 1182(w), 1085(m), 1016(m), 800(s), 486(s) cm^{-1} .

45. Decakis(cyclohexylthio)biphenyl (149)

Sodium cyclohexylthiolate 1.65g (12 mmols), prepared from cyclohexylthiol and sodium according to the method of experiment 16 (Method A), was reacted with decafluorobiphenyl 0.200g (0.6 mmols) in DMEU (30 ml), at 60°C, for 5 days and worked up according to the method of experiment

43. The yellow oil was purified by gravity column, pet. ether (40-60°C)/diethyl ether [20:1] to give a pale yellow foam 0.4565g (58.9%). TLC R_f = 0.50 pet. ether (40-60°C)/diethyl ether [20:1]; δ_H (200 MHz, $CDCl_3$) 3.50-3.31 (m, 10H, 10 x ArSCH), 1.99-0.88 (m, 100H, 50 x CH_2); δ_C (50 MHz, $CDCl_3$) 147.35(s), 146.63(s), 145.48(s), 143.50(s), 140.81(s), 49.83(d), 49.66(d), 49.53(d), 48.63(d), 48.47(d), 47.62(d), 33.27(t), 33.09(t), 32.87(t), 32.82(t), 32.60(t), 26.10(t), 25.96(t), 25.81(t); ν_{max} (KBr disc) 2927(s), 2851(s), 1448(m), 1380(w), 1338(w), 1289(w), 1261(m), 996(m), 737(w) cm^{-1} .

46. Decakis(cyclopentylthio)biphenyl (150)

Sodium cyclopentylthiolate 1.11g (9.0 mmols), prepared from cyclopentylthiol and sodium according to the method of experiment 16 (Method A), is reacted with decafluorobiphenyl 0.150g (0.45 mmols) in DMEU (30 ml), at 60°C, for 5 days and worked up according to the method of experiment 43. The yellow oil was purified by gravity column, pet. ether (40-60°C)/diethyl ether [15:1] to give yellow crystals which are recrystallised from 1,4-dioxane/chloroform/methanol 0.214g (34.7%) m.pt. 221-224°C; TLC R_f = 0.58, pet. ether (40-60°C)/diethyl ether [15:1]; δ_{H} (200 MHz, CDCl₃) 4.05-3.68 (m, 10H, 10 x ArSCH), 1.80-1.30 (m, 80H, 40 x CH₂); δ_{C} (50 MHz, CDCl₃) 148.03(s), 146.94(s), 145.72(s), 144.27(s), 141.57(s), 49.36(d), 49.14(d), 48.98(d), 48.85(d), 48.42(d), 48.15(d), 33.51(t), 33.42(t), 33.25(t), 32.99(t), 32.90(t), 32.76(t), 24.99(t), 24.89(t), 24.83(t), 24.74(t); ν_{max} (KBr disc) 2950(s), 2865(s), 1447(m), 1379(w), 1316(m), 1288(m), 1236(m), 1126(w), 1082(w), 954(w), 934(w), 902(w) cm⁻¹.

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47. Decakis(phenylthio)benzophenone (152)

Sodium thiophenolate 2.0g (15.1 mmols), prepared from thiophenol and sodium according to the method of experiment 16 (Method A), was dissolved in DMEU (30 ml) and the solution degassed. Perfluorobenzophenone 0.274g (0.78 mmols) was then added and the mixture degassed again and stirred, at room temperature, for 2 hours. Toluene (200 ml) was then added and the organic layer washed with water (10 x 100 ml). After the solvent was removed the yellow oil was purified by a gravity column, toluene to yield a yellow powder which was recrystallised from chloroform/methanol to yield yellow crystals 0.9028g (94.5%) m.pt. 238-240°C; TLC R_f = 0.58 toluene. Found: (recrystallised from chloroform/acetic acid) C, 64.16; H, 3.56; S, 23.61%. $C_{73}H_{50}S_{10}O:CHCl_3$ requires C, 64.28; H, 3.69; S, 23.16%; δ_H (200 MHz, CD_2Cl_2) 7.70-7.20 (m, 40H, 40 x ArH), 6.80-6.70 (m, 10H, 10 x ArH); δ_C (50 MHz, CD_2Cl_2) 191.94(s), 151.96(s), 151.13(s), 149.98(s), 139.86(s), 138.11(s), 137.72(s), 137.64(s), 129.37(d), 129.27(d), 128.71(d), 128.15(d), 127.60(d), 126.74(d), 126.43(d); ν_{max} (KBr disc) 3071 (m), 3056(m), 1582(s), 1478(s), 1458(w), 1439(s), 1192(m), 1080(w), 1024(m), 999(w), 735(s), 698(m), 687(s) cm^{-1} ; FAB MS m/e (M+H)⁺ 1263, 1153, 1076, 1045, 645.

48. Decakis(*p*-tolylthio)benzophenone (153)

Sodium *p*-tolylthiolate 1.71g (11.7 mmols), prepared from *p*-tolylthiol and sodium according to the method of experiment 16 (Method A), was reacted with perfluorobenzophenone 0.212g (0.59 mmols) in DMEU (30 ml), at room temperature, for 2 hours and worked up according to the method of experiment

43. The yellow oil was purified by gravity column, toluene/pet. ether (40-60° C) [7:3] and the yellow powder was recrystallised from diethyl ether to give

yellow crystals 0.2921g (35.6%) m.pt. 126-127°C; TLC R_f = 0.28,

toluene/pet. ether (40-60°C) [7:3]; Found: C, 71.25; H, 5.14; S, 23.14%

$C_{83}H_{70}S_{10}O$ requires C, 71.04; H, 4.99; S, 22.82%; δ_H (200 MHz, $CDCl_3$) 6.90-

6.53 (m, 40H, 40 x ArH), 2.27-2.22 (2 x s, 30H, 30 x ArCH₃); δ_C (50 MHz,

$CDCl_3$), 192.36(s), 151.30(s), 151.03(s), 149.48(s), 139.62(s), 135.80(s),

135.46(s), 135.44(s), 134.36(s), 134.11(s), 134.07(s), 129.50(d), 129.42(d),

129.01(d), 128.43(d), 127.75(d), 21.05(q); ν_{max} (KBr disc) 3019 (w),

2921(m), 1655(m), 1491(s), 1474(w), 1466(w), 1458(w), 1449(w), 1183(w),

1017(w), 799(s), 486(m) cm^{-1} .

49. Decakis(*m*-tolylthio)benzophenone (154)

Sodium *m*-tolylthiolate 2.0g (15.1 mmols), prepared from *m*-tolylthiol and sodium according to the method of experiment 16 (Method A), was reacted with perfluorobenzophenone 0.284g (0.78 mmols) in DMEU (30 ml), at room temperature, for 2 hours and worked up according to the method of experiment 43. The yellow oil was purified by gravity column, toluene/pet. ether (40-60°C) [7:3] and the yellow powder was recrystallised from 1,4-dioxane/hexane to give yellow crystals (1,4-dioxane adduct) 0.4373g (40%) m.pt. 121-122°C. TLC R_f = 0.23, toluene/pet. ether (40-60°C) [7:3]; Found: C, 70.19; H, 5.23% C₈₃H₇₀S₁₀O: 1½C₄H₈O₂C, 69.62; H, 5.35%; δ_H (200 MHz, CDCl₃) 6.99-6.36 (m, 40H, 40 x ArH), 2.21-2.15 (2 x s, 30H, 10 x ArCH₃); δ_C (50 MHz, CDCl₃) 191.98(s), 151.98(s), 150.67(s), 149.34(s), 140.02(s), 138.39(s), 138.30(s), 137.54(s), 128.79(d), 128.52(d), 128.23(d), 128.17(d), 126.80(d), 126.71(d), 126.64(d), 124.99(d), 124.58(d), 124.38(d), 21.46(q), 21.41(q), 21.38(q); ν_{max} (KBr disc) 3052(w), 2921(m), 1655(w), 1649(w), 1591(s), 1474(m), 1458(w), 1194(w), 1080(w), 853(w), 770(s), 687(s), cm⁻¹.

50. Decakis(3,5-dimethylphenylthio)benzophenone (155)

Sodium 3,5-dimethylphenylthiolate 2.0g (12.5 mmols), prepared from 3,5-dimethylphenylthiol and sodium according to the method of experiment 16 (Method A), was reacted with perfluorobenzophenone 0.226g (0.62 mmols) in DMEU (30 ml), at room temperature, for 2 hours and worked up according to the method of experiment 43. The yellow oil was purified by recrystallisation from chloroform/methanol/diethyl ether to give yellow crystals 0.747g (78%) m.pt. 215-216°C. TLC R_f = 0.29, toluene/pet. ether (40-60°C) [6:4]; Found: C, 72.48; H, 5.82; S, 20.98% C₉₃H₉₀S₁₀O requires C, 72.37; H, 5.83; S, 20.75%; δ_H (200 MHz, CDCl₃) 6.58 (s, 20H, 20 x ArH), 6.37-6.33 (m, 10H, 10 x ArH), 2.09-2.06 (3 x s, 60H, 20 x ArCH₃); δ_C (50 MHz, CDCl₃) 191.76(s), 152.79(s), 150.25(s), 149.04(s), 140.74(s), 137.93(s), 137.87(s), 137.42(s), 137.13(s), 127.75(d), 127.49(d), 125.73(d), 125.23(d), 21.27(q); ν_{max} (KBr disc) 3031(m), 3002(m), 2948(m), 2915(s), 2859(m), 1601(s), 1580(s), 1460(m), 1375(w), 1190(w), 837(s), 681(s) cm⁻¹.

51. Decakis(3,4-dimethylphenylthio)benzophenone (156)

Sodium 3,4-dimethylphenylthiolate 1.28g (8 mmols), prepared from 3,4-dimethylphenylthiol and sodium according to the method of experiment 16 (Method A), was reacted with perfluorobenzophenone 0.145g (0.40 mmols) in DMEU (30 ml), at room temperature, for 2 hours and worked up according to the method of experiment 43. The yellow oil was purified by gravity column, pet. ether (40-60°C)/diethyl ether [7:3] to yield a yellow powder 0.4091g (66.3%) m.pt. 95-100°C. TLC R_f = 0.37, pet. ether/diethyl ether [7:3]; Found: C, 72.49; H, 6.27% $C_{93}H_{90}S_{10}O$ requires C, 71.63; H, 5.78%; δ_H (200 MHz, $CDCl_3$) 6.79 - 6.28 (m, 30H, 30 x ArH), 2.15 - 2.03 (4 x s, 60H, 20 x ArCH₃); δ_C (50 MHz, $CDCl_3$) 192.18(s), 151.52(s), 150.88(s), 149.08(s), 140.30(s), 136.75(s), 136.62(s), 134.59(s), 134.06(s), 133.97(s), 133.84(s), 129.92(d), 129.80(d), 129.59(d), 129.08(d), 128.97(d), 125.66(d), 125.22(d), 19.75(q), 19.66(q), 19.31(q); ν_{max} (KBr disc) 3009 (m), 2965(m), 2917(s), 2859(m), 1487(s), 1449(s), 1383(m), 1285(m), 1184(m), 1140(m), 1129(m), 1019(m), 992(m), 880(m), 804(s), 700(m), 546(m), 434(m), cm^{-1} .

52. Decakis(3,4,5-trimethylphenylthio)benzophenone (157)

Sodium 3,4,5-trimethylphenylthiolate 1.23g (7 mmols), prepared from 3,4,5-trimethylphenylthiol and sodium according to the method of experiment 16 (Method A), was reacted with perfluorobenzophenone 0.150g (0.40 mmols) in DMEU (30 ml), at room temperature, for 2 hours and worked up according to the method of experiment 43. The yellow oil was purified by gravity column, pet. ether (40-60°C)/diethyl ether [8:2] and recrystallisation from pet. ether (40-60°C)/diethyl ether, to yield yellow crystals 0.350g (52.6%) m.pt. 185-190°C. TLC R_f = 0.25, pet. ether (40-60°C)/diethyl ether [8:2]; Found:

C, 73.26; H, 6.33; S, 19.21% $C_{103}H_{110}S_{10}O$ requires C, 73.48; H, 6.53; S, 19.02%; δ_H (200 MHz, $CDCl_3$) 6.80-6.18 (m, 20H, 20 x ArH), 2.37-1.89 (m, 90H, 30 x $ArCH_3$); δ_C (50 MHz, $CDCl_3$) 191.12(s), 160.45(s), 153.33(s), 150.72(s), 150.01(s), 149.15(s), 148.91(s), 146.37(s), 139.90(s), 136.55(s), 136.52(s), 136.32(s), 134.09(s), 133.85(s), 133.58(s), 133.24(s), 133.18(s), 133.02(s), 132.52(s), 132.49(s), 132.52(s), 132.49(s), 132.40(s), 132.22(s), 130.94(s), 128.92(d), 127.67(d), 127.58(d), 127.16(d), 126.71(d), 126.60(d), 126.49(d), 20.71(q), 20.58(q), 20.50(q), 20.30(q), 15.27(q), 15.04(q), 14.96(q), 14.83(q); ν_{max} (KBr disc) 2970 (m), 2914(s), 2860(m), 1656(w), 1586(m), 1570(m), 1474(s), 1442(s), 1400(m), 1376(m), 1353(m), 1285(w), 1233(w), 1193(m), 1166(w), 996(w), 936(w), 882(m), 850(m), 700(w), 554(w) cm^{-1} .

53. Decakis(*p*-*t*-butylphenylthio)benzophenone (158)

To a solution of sodium *p*-*t*-butylphenylthiolate in DMEU (30 ml), prepared from *p*-*t*-butylthiophenol 1.38g (8.3 mmols) and sodium hydride (95%) 0.230g (9.1 mmols) according to the method of experiment 16 (Method B), was added perfluorobenzophenone 0.150g (0.40 mmols) and stirred at room temperature, for 2 hours. It was then worked up according to the method of experiment 43. The yellow oil was purified by gravity column diethyl ether/pet. ether (40-60°C) [1:9] to yield yellow crystals 0.2747g (36.4%) m.pt. 164-166°C. TLC $R_f = 0.35$, diethyl ether/pet. ether (40-60°C) [1:9]; Found: C, 74.63; H, 7.18; S, 17.43%. $C_{113}H_{130}OS_{10}$ requires C, 74.42; H, 7.13; S, 17.56%; δ_H (200 MHz, $CDCl_3$) 7.14-6.60 (m, 40H, 40 x ArH), 1.27-1.22 (3 x s, 90H, 10 x $C(CH_3)_3$); δ_H (50 MHz, $CDCl_3$) 192.09(s), 152.40(s), 150.56(s), 149.18(s), 148.83(s), 148.62(s), 148.46(s), 140.06(s), 134.55(s), 134.42(s), 134.30(s), 127.67(d), 127.35(d), 126.79(d), 126.15(d), 125.60(d), 34.37(s), 34.32(s), 31.35(q), 31.29(q); ν_{max} (KBr disc) 2961(s), 2903(m), 2869(m), 1497(s), 1460(m), 1397(w), 1362(w), 1269(m), 1117(m), 1013(m), 820(s), 544(m) cm^{-1} .

54. Decakis(*p*-methoxyphenylthio)benzophenone (159)

To a solution of sodium *p*-methoxyphenylthiolate in DMEU (30 ml), prepared from *p*-methoxythiophenol 3.97g (28.3 mmols) and sodium hydride (95%) 0.72g (30 mmols) according to the method of experiment 16 (Method B), was added perfluorobenzophenone 0.500g (1.38 mmols) and stirred, at room temperature, for 2 hours. It was then worked up according to the method of experiment 43. The yellow oil was purified by gravity column, chloroform to yield a yellow powder 0.9194g (42.5%) m.pt. 190°C. TLC R_f = 0.20 chloroform; Found: C, 63.73; H, 4.64%; $C_{83}H_{70}O_{11}S_{10}$ requires C, 63.76; H, 4.48%; δ_H (200 MHz, $CDCl_3$) 7.23 (s, 4H, 4 x ArH), 7.02-6.98 (m, 8H, 8 x ArH), 6.70-6.50 (m, 28H, 28 x ArH), 3.74-3.70 (3 x s, 30H, 10 x $ArOCH_3$); δ_C (50 MHz, $CDCl_3$) 192.78 (s), 158.34(s), 158.14(s), 158.09(s), 150.90(s), 149.80(s), 149.42(s), 139.43(s), 131.14(d), 130.58(d), 129.84(d), 128.58(d), 128.10(d), 128.08(d), 114.45(d), 114.25(d), 55.12(q), 55.06(q); ν_{max} (KBr disc) 3002(w), 2938(w), 2834(w), 1593(m), 1493(s), 1460(m), 1289(m), 1246(s), 1175(m), 1030(m), 820(m) cm^{-1} .

55. Decakis(*p*-hydroxyphenylthio)benzophenone (160)

Decakis(*p*-methoxyphenylthio)benzophenone 0.500g (0.32 mmols) was dissolved in dichloromethane (20 ml) and cooled to -78°C under a nitrogen atmosphere. BBr_3 (1M) 16 ml (16 mmols) was then added and the mixture left to stir overnight at room temperature. Water was then carefully added (1 drop at a time) until no more fumes are given off. The blue/green solid was filtered off, dissolved in acetone and filtered again. The solvent was then dried with sodium sulphate and acetone removed and the remaining oil purified by a gravity column ethyl acetate/methanol [8:2] to give a yellow powder 0.236g (51.9%). TLC $R_f = 0.54$, ethyl acetate/methanol [8:2]; δ_{H} (200 MHz, CD_3OD) 7.24-6.41 (m, 40H, 40 x ArH); δ_{C} (50 MHz, CD_3OD) 194.04(s), 157.50(s), 157.25(s), 152.52(s), 150.82(s), 150.45(s), 140.89(s), 132.70(d), 131.93(d), 131.37(d), 129.91(d), 129.21(d), 128.54(s), 128.33(s), 128.24(s), 126.30(d), 116.94(d), 116.87(d); ν_{max} (KBr disc) 3384(s), 1638(w), 1599(s), 1584(s), 1492(s), 1429(m), 1358(w), 1235(s), 1169(s), 1099(w), 1009(w), 821(s), 512(w) cm^{-1} .

56. Decakis(5-indanethio)benzophenone (161)

To a solution of sodium 5-indanethiolate in DMEU (30 ml), prepared from 5-indanethiol 0.925g (6.17 mmols) and sodium hydride (95%) 0.171g (6.79 mmols) according to the method of experiment 16 (Method B) was added perfluorobenzophenone 0.110g (0.31 mmols) and stirred, at room temperature, for 2 hours. It was then worked up according to the method of experiment 43. The yellow oil was purified by gravity column, pet. ether (40-60°C)/diethyl ether [7:3] to yield a yellow foam 0.2650g (51.4%). TLC R_f = 0.34, pet. ether/diethyl ether [7:3]. Found: C, 73.87; H, 5.58; S, 19.44% $C_{103}H_{90}OS_{10}$ requires C, 74.36; H, 5.41; S, 19.25%; δ_H (200 MHz, $CDCl_3$) 7.02-6.35 (m, 30H, 30 x ArH), 2.78-2.67 (m, 40H, 20 x $ArCH_2$), 2.08-1.88 (m, 20H, 10 x CH_2); δ_C (50 MHz, $CDCl_3$) 192.44(s), 151.48(s), 149.24(s), 144.66(s), 144.55(s), 141.92(s), 141.83(s), 141.66(s), 140.79(s), 135.23(s), 135.13(s), 126.27(d), 125.86(d), 125.73(d), 124.46(d), 124.31(d), 124.10(d), 123.82(d), 32.72(t), 32.41(t), 25.28(t); ν_{max} (KBr disc) 2942(s), 2840(s), 1655(m), 1649(w), 1597(m), 1474(s), 1435(m), 1404(m), 1285(w), 1258(w), 1192(w), 1177(w), 1097(w), 860(w), 806(m) cm^{-1} .

57. Decakis(2-naphthylthio)benzophenone (162)

Sodium 2-naphthylthiolate, 2.01g (11 mmols), prepared from 2-naphthylthiol and sodium according to the method of experiment 16 (Method A) was reacted with perfluorobenzophenone 0.1986g (0.55 mols) in DMEU (30 ml), at room temperature, for 3 hours and worked up according to the method of experiment 43. The yellow oil was purified by gravity column, pet. ether (40-60°C)/toluene [2:8] to yield a yellow foam 0.7217g (74.7%) m.pt. 199-202 °C. TLC R_f = 0.34, pet. ether (40-60°C)/toluene [2:8]; Found: C, 77.13; H, 4.02; S, 18.43% $C_{113}H_{70}S_{10}O$ requires C, 76.96; H, 3.97; S, 18.16%; δ_c (200 MHz, $CDCl_3$) 7.52-6.61 (m, 70H, 70 x ArH); δ_c (50 MHz, $CDCl_3$) 192.40(s), 151.94(s), 151.02(s), 149.96(s), 140.20(s), 138.15(s), 135.20(s), 134.76(s), 134.63(s), 133.88(s), 133.79(s), 133.69(s), 132.11(s), 132.00(s), 130.16(s), 129.06(d), 128.74(d), 128.40(d), 128.00(d), 127.90(d), 127.77(d), 127.58(d), 127.48(d), 127.40(d), 126.98(d), 126.83(d), 126.60(d), 126.32(d), 126.25(d), 126.20(d), 126.12(d), 125.95(d); ν_{max} (KBr disc) 3050(s), 1624(m), 1588(m), 1501(s), 1458(w), 1453(w), 1192(m), 1132(m), 941(m), 849(m), 808(s), 741(s), 473(m) cm^{-1} .

58. Decakis(cyclopentylthio)benzophenone (163)

Sodium cyclopentylthiolate, 1.75g (14.1 mmols) prepared from cyclopentylthiol and sodium according to the method of experiment 16 (Method A), was reacted with perfluorobenzophenone 0.255g (0.71 mmols) in DMEU (30 ml), at room temperature, for 3 hours and worked up according to the method of experiment 43. The yellow oil was purified by gravity column, pet. ether (40-60°C)/diethyl ether [10:1] to yield yellow crystals from diethyl ether/methanol 0.299g (39.0%) m.pt. 193-194°C (dioxane clathrate). TLC R_f = 0.47 pet. ether (40-60°C)/diethyl ether [10:1]; Found: C, 63.13; H, 7.95; S, 25.56%, $C_{63}H_{90}S_{10}O:C_4H_8O_2$, C, 63.31; H, 7.72; S, 25.20%; δ_H (200 MHz, $CDCl_3$) 4.10-3.65 (m, 10H, 10 x $ArSCH$), 1.80-1.45 (m, 80H, 40 x CH_2); δ_C (50 MHz, $CDCl_3$) 189.99 (s), 150.94(s), 147.85(s), 147.76(s), 140.37(s), 50.25(d), 48.98(d), 48.70(d), 33.12(t), 32.96(t), 32.90(t), 25.14(t), 24.96(t), 24.87(t); ν_{max} (KBr disc) 2955 (s), 2867(s), 1686(m), 1466(w), 1458(w), 1449(m), 1316(w), 1281(m), 1237(m), 1177(w), 993 (w) cm^{-1} ; FAB MS m/e $(M+H)^+$ 1113, 1080, 1013, 943, 875, 605, 535.

59. Decakis(cyclohexylthio)benzophenone (164)

To a solution of sodium cyclohexylthiolate in DMEU, prepared from cyclohexylthiol 0.9616g (8.3 mmols) and sodium hydride 95% 0.210g (8.3 mmols) according to the method of experiment 16 (Method B), was added perfluorobenzophenone 0.150g (0.41 mmols) and stirred, at room temperature, for 2 hours. It was then worked up according to the method of experiment 43. The yellow oil was purified by gravity column toluene/pet. ether (40-60°C) [1:1] to yield yellow crystals 0.2095g (38.2%) m.pt. 200-203°C. TLC R_f = 0.52, toluene/pet. ether (40-60°C) [1:1]; δ_H (200 MHz, $CDCl_3$) 3.51-3.20 (m, 10H, 10 x ArSCH), 1.70-1.22 (m, 100H, 50 x CH_2); δ_C (50 MHz, $CDCl_3$) 151.59(s), 147.48(s), 139.40(s), 50.10(d), 49.67(d), 49.45(d), 32.98(t), 32.79(t), 32.72(t), 26.43(t), 26.07(t), 25.98(t), 25.80(t); ν_{max} (KBr disc) 2928(s) 2851(s), 1449(m), 1339(w), 1260(m), 1202(w), 997(m), 737(w), cm^{-1} .

60. Decakis(10-(*S*)-camphorthio)benzophenone (165)

Sodium 10-(*S*)-camphorthiolate 2.02g (9.8 mmols), prepared from 10-(*S*)-mercaptocamphor and sodium according to the method of experiment 16 (Method A), was reacted with perfluorobenzophenone 0.1967g (0.54 mmols) in DMEU (30 ml), at room temperature, for 3 hours and worked up according to the method of experiment 43. The yellow oil was purified by flash chromatography, diethyl ether, to yield a yellow powder 0.440g (41%) m.pt. 185-189°C. TLC R_f = 0.15 diethyl ether; Found: C, 67.88; H, 7.57; S, 16.10% $C_{113}H_{150}O_{11}S_{10}$ requires C, 67.73; H, 7.49; S, 15.98%; δ_H (200 MHz, $CDCl_3$) 3.41-2.86 (m, 20H), 2.40-1.22 (m, 70H, 70 x alkylH), 1.10-0.90 (m, 60H, 20 x CH_3); δ_C (50 MHz, $CDCl_3$) 216.80(s), 216.67(s), 216.47(s), 151.90(s), 150.56(s), 150.31(s), 140.34(s), 140.24(s), 139.11(s), 61.31(s), 60.82(s), 47.93(s), 43.40(d), 43.04(t), 42.90(t), 36.28(t), 35.59(t), 35.00(t), 26.95(t), 26.54(t), 26.34(t), 25.86(t), 20.64(q), 20.43(q), 20.26(q), 20.10(q), 19.99(q); ν_{max} (KBr disc) 2959(s), 2885(m), 1743(s), 1468(w), 1453(m), 1417(m), 1390(w), 1373(w), 1295(w), 1279(w), 1197(w), 1062(w), 1048(m), 1028(w) cm^{-1} .

61. Decakis((+)-1-phenylethylthio)benzophenone (166)

To a solution of (+)-1-phenylethylthiolate in DMEU (30 ml), prepared from (+)-1-phenylethylthiol 1g (7.25 mmols) and sodium hydride (95%), 0.183g (7.63 mmols) according to the method of experiment 16 (Method B), was added perfluorobenzophenone 0.131g (0.36 mmols) and stirred, at room temperature, for 2 hours. It was then worked up according to the method of experiment 43. The yellow oil was purified by gravity column, pet. ether (40-60°C)/diethyl ether [8:2] to yield a yellow powder 0.125g (22.5%). TLC R_f = 0.30, pet. ether/diethyl ether [8:2]; Found: C, 72.35; H, 5.92; S, 20.72%. $C_{93}H_{90}OS_{10}$ requires C, 72.37; H, 5.83; S, 20.75%; δ_H (200 MHz, $CDCl_3$) 7.47-7.06 (bm, 50H, 50 x ArH), 4.93-4.09 (bm, 10H, 10 x ArCH(CH_3)S), 1.56-0.85 (bm, 30H, 10 x ArCH(CH_3)S); δ_C (50 MHz, $CDCl_3$) 142.97(s), 128.34(d), 128.25(d), 127.78(d), 127.55(d), 127.13(d), 51.29(bd), 50.62(d), 22.86(bq); ν_{max} (KBr disc) 3059(w), 3026(w), 2962(m), 2920(m), 2862(w), 1686(w), 1491(m), 1452(s), 1372(w), 1177(w), 1042(m), 1026(s), 990(w), 764(s), 696(s), 668(w), 529(w) cm^{-1} .

62. Decakis(phenoxy)benzophenone (167)

Sodium phenolate 1.74g (15 mmols), prepared from phenol and sodium hydride (95%) according to the method of experiment 17 was reacted with decafluorobenzophenone 0.272g (0.75 mmols) in HMPA (30 ml) at 60°C, for 1 month and worked up according to the method of experiment 26. The pale yellow oil was purified by gravity column diethyl ether/pet. ether (40-60°C) [4:6] to give a white solid which was recrystallised from diethyl ether/methanol to yield white crystals 0.345g (41.7%) m.pt. 137-138°C. TLC R_f = 0.55 diethyl ether/pet. ether (40-60°C) [4:6]; δ_H (200 MHz, $CDCl_3$) 7.29-6.67 (m, 50H, 50 x ArH); δ_C (50 MHz, $CDCl_3$) 157.61(s), 157.31(s), 156.47(s), 147.23(s), 144.00(s), 136.40(s), 129.61(d), 129.11(d), 129.04(d), 123.47(d), 122.40(d), 122.20(d), 117.86(d), 115.88(d), 115.45(d), 108.52(d); ν_{max} (KBr disc) 3058(w), 3040(w), 1591(s), 1489(s), 1476(s), 1456(m), 1441(s), 1252(m), 1207(s), 1162(m), 1072(w), 1053(m), 1024(w), 965(m), 749(s), 686(s) cm^{-1} ; FAB MS m/e (M^+) 1102, 1099, 1009, 993, 538, 446.

63. Attempted formation of Decafluorodiphenyldioxolane

Using ethylene glycol and PTSA

A mixture of perfluorobenzophenone 1g (2.76 mmols) cyclohexane (4½ ml), ethylene glycol 0.38g (6.1 mmols) and PTSA 0.17g (*ca.* 0.1 mmols) was refluxed with stirring, in a Dean-Stark apparatus for 5 days. The contents are neutralised with powdered sodium acetate 55 mg (0.67 mmols) and the solvent removed under reduced pressure after filtration. TLC and ¹H NMR (90 MHz) showed starting material only present.

Using Bis(trimethylsiloxy)ethane and TMSOTf

To a stirring solution of trimethylsilyltriflate 22mg (0.1 mmols) in dichloromethane (1 ml) was added bis(trimethylsiloxy)ethane 0.569g (2.90 mmols) and perfluorobenzophenone 1g (2.76 mmols) at -78°C under a nitrogen atmosphere and was stirred at -78°C for 3 hours and then quenched by addition of dry pyridine (0.2 ml). At the same temperature it was poured into saturated NaHSO₃ aqueous solution (15 ml) and extracted with ether (3 x 15 ml). The extracts were then dried over 1:1 mixture of NaHCO₃:Na₂SO₃ and the solvent removed. TLC and ¹H NMR (90 MHz) showed starting material only present.

64. Decakis(phenylthio)benzohydrol (169)

Sodium phenylthiol, 2.0g (15.2 mmols) prepared from thiophenol and sodium according to the method of experiment 16 (Method A), was reacted with decafluorobenzohydrol 0.2771g (0.76 mmols) in DMEU (30 ml), at room temperature, for 5 days and worked up according to the method of experiment 43. The yellow oil was purified by gravity column, toluene, the resulting yellow solid was recrystallised from chloroform/methanol to yield yellow crystals 0.1353g (14.1%) m.pt. 131-135°C. TLC R_f = 0.52, toluene; δ_H (200 MHz, $CDCl_3$) 7.17-6.96 (m, 40H, 40 x ArH), 6.71-6.63(m, 11H, 10 x ArH, ArCH(OH)Ar); δ_C (50 MHz, $CDCl_3$) 152.04(s), 151.19(s), 150.04(s), 139.92(s), 138.18(s), 137.78(s), 137.71(s), 129.43(d), 129.34(d), 128.79(d), 128.21(d), 127.66(d), 126.80(d), 126.49(d); ν_{max} (KBr disc) 3448(bs), 3054(s), 1734(w), 1580(m), 1476(s), 1438(m), 1024(m), 734(s), 698(m), 686(m) cm^{-1} .

65. Decakis(β -naphthylthio)benzohydrol (170)

Sodium β -naphthylthiolate 5.14g (28.2 mmols), prepared from β -naphthylthiol and sodium according to the method of experiment 16 (Method A) was reacted with decafluorobenzohydrol 0.5g (1.37 mmols) in DMEU (30 ml), according to the method of experiment 43. The yellow oil was purified by gravity column, pet. ether (40-60°C)/toluene [3:7] to yield a yellow foam 0.782g (32.3%). TLC R_f = 0.35 pet. ether (40-60°C)/toluene [3:7]; δ_H (200 MHz, $CDCl_3$) 7.95 (bs, 1H, ArCH(OH)Ar), 7.68-6.52 (m, 71H, 70 x ArH, ArCH(OH)Ar); δ_C (50 MHz, $CDCl_3$) 149.64(s), 149.00(s), 148.31(s), 141.07(s), 137.02(s), 135.81(s), 134.60(d), 135.17(s), 133.91(s), 133.79(s), 133.60(s), 133.46(s), 133.26(s), 133.18(s), 133.02(s), 131.98(s), 131.69(s), 131.59(s), 130.37(d), 129.95(d), 128.67(d), 128.25(d), 127.67(d), 127.52(d), 127.38(d), 127.04(d), 126.77(d), 126.50(d), 126.37(d), 126.24(d), 125.90(d), 125.55(d); ν_{max} (KBr disc) 3520(m), 3049(m), 1654(m), 1624(m), 1587(s), 1500(s), 1452(m), 1340(w), 1267(w), 1237(w), 1195(m), 1132(m), 1067(w), 1008(w), 942(m), 848(s), 809(s), 759(m), 740(s), 471(s) cm^{-1} .

66. Decakis(cyclohexylthio)benzohydrol (171)

Sodium cyclohexylthiolate, 3.0g (21.7 mmols), prepared from cyclohexyl thiol and sodium according to the method of experiment 16 (Method A), was reacted with decafluorobenzohydrol 0.396g (1.09 mmols) in DMEU (30 ml), at 60°C, for 5 days and worked up according to the method of experiment 43. The yellow oil was purified by gravity column, pet. ether (40-60°C)/diethyl ether [15:1]. This gave a yellow solid which was recrystallised from diethyl ether/pet. ether (40-60°C) yielding yellow crystals 352 mg (24.4%). m.pt. 195-197°C. TLC R_f = 0.37, pet. ether (40-60°C)/diethyl ether [20:1]; δ_H (200 MHz, $CDCl_3$) 10.26 (s, 1H, ArCH(OH)Ar), 6.95 (s, 1H, ArCH(OH)Ar), 3.37-3.11 (m, 10H, 10 x ArSCH) 1.80-1.18 (m, 100H, 50 x CH_2); δ_C (50 MHz, $CDCl_3$) 191.26(d), 140.04(s), 137.58(s), 50.71(d), 49.83(d), 33.31(t), 33.18(t), 26.00(t), 25.59(t); ν_{max} (KBr disc) 2927(s), 2851(s), 1447(m), 1338(w), 1298(w), 1260(m), 1201(w), 1096(w), 996(m), 887(w), 737(w) cm^{-1} .

67. Attempted formation of Decakis(cyclopentylthio)benzohydrol

Sodium cyclopentylthiolate, 1.6g (12.9 mmols) prepared from cyclopentylthiol and sodium according to the method of experiment 16 (Method A), was reacted with decafluorobenzohydrol 0.235g (0.65 mmols) in DMEU (30 ml) at 60°C for 5 days and worked up according to the method of experiment 43. The yellow oil was purified by gravity column, pet. ether (40-60°C)/diethyl ether [15:1]. To yield a yellow oil which contained 4 spots by TLC pet. ether (40-60°C)/diethyl ether [15:1]. No product could be isolated and no further analysis was carried out.

68. bis-(pentafluorophenyl)methanemesylate (174)

To a stirring solution of decafluorobenzohydrol 1.0g (2.75 mmols) in pyridine (20 ml), under a nitrogen atmosphere, was added mesyl chloride 0.472g (3.3 mmols). After 2 hours the moisture was added to iced water and extracted with dichloromethane (3 x 50ml). This was then washed with 10% sulphuric acid (2 x 25 ml) and then brine (2 x 50 ml). The organic layer was dried with sodium sulphate and the solvent removed. The white solid was purified by flash column chromatography, it was first flushed with pet. ether (40-60°C) to remove (A) 0.3783g, (36.2%) [based on amount of mesylate formed] and then with chloroform to remove (B) 0.6940g (57.4%).

(A) (175) $C_{13}H ClF_{10}$: TLC R_f = 0.68, pet. ether (40-60°C)/diethyl ether [7:3]; δ_H (200 MHz, $CDCl_3$) 6.63(s, 1H, $ArCHClAr$); MS m/e 384 ($M^+ ^{37}Cl$), 382 ($M^+ ^{35}Cl$), 347, 309, 278, 247, 228, 141, 117, 93, 69, 31.

(B) (174) $C_{14}H_4F_{10}O_3S$: TLC R_f = 0.28, pet. ether (40-60°C)/diethyl ether [7:3]; δ_H (200 MHz, $CDCl_3$) 7.24 (s, 1H, $ArCH(OSO_2CH_3)Ar$), 3.15 (s, 3H, $ArCH(OSO_2CH_3)Ar$); MS m/e 442 M^+ 347, 278, 195, 143, 107, 79, 57, 41.

69. Attempted Synthesis of bis(pentafluorophenyl)methane (172)
via Reduction of bis(pentafluorophenyl)methane mesylate (174)

A. Reduction with lithium aluminium hydride

To a solution of bis(pentafluorophenyl)methane mesylate 0.472g (1.07 mmols) in diethyl ether (20 ml) was added lithium aluminium hydride 0.203g (5.34 mmols) and stirred for 2 hours. The reaction mixture was then carefully quenched with ethyl acetate until no more gas was evolved, it was then taken up in diethyl ether and washed with 10% H_2SO_4 (2 x 50 ml) and then with brine (2 x 50 ml). The solvent was removed and the resulting product purified by flash column chromatography to yield a white solid 0.2692g (67.8%); δ_{H} (90 MHz, CDCl_3) 7.15-6.60 (m, 2H, 2 x ArH), 4.10 (bs, 2H, ArCH_2Ar).

B. Reduction with sodium borohydride in THF

To a solution of bis(pentafluorophenyl)methane mesylate 0.694g (1.57 mmols) in THF (20 ml) was added sodium borohydride 60 mg (1.59 mmols) stirred for 4 hours. The reaction mixture was then added to water and extracted with diethyl ether (3 x 30 ml). The organic layer was dried with sodium

sulphate and the solvent removed to give back the starting material as a white solid TLC

$R_f = 0.28$ pet. ether (40-60°C)/diethyl ether [7:3]; δ_H (90 MHz, $CDCl_3$) 7.40 (s, 1H, $ArCH(OSO_2CH_3)Ar$), 3.15 (s, 3H, $ArCH(OSO_2CH_3)Ar$).

C. Reduction with sodium borohydride in sulpholane

To a solution of bis(pentafluorophenyl)methane mesylate 0.694g (1.57 mmols) in sulpholane was added sodium borohydride 180 mg (4.76 mmols) and the mixture refluxed for 4 hours. The resulting mixture was then added to toluene and washed with water (30 ml x 3). The toluene was then removed and the oil dissolved in diethyl ether and dried over sodium sulphate and the solvent removed to yield a white solid. δ_H (90 MHz, $CDCl_3$) 7.15-6.60 (m, 2H, 2 x ArH), 4.10 (bs, 2H, $ArCH_2Ar$).

D. Reduction with lithium aluminium hydride of
bis(pentafluorophenyl)methylchloride (175)

To a solution of bis(pentafluorophenyl)methyl chloride 1.335g (3.5 mmols) in diethyl ether (30 ml) was added lithium aluminium hydride 0.665g (17.5 mmols) and stirred for 2 hours. It was then worked up according to the method of experiment A to yield a white solid. δ_H (90 MHz, $CDCl_3$) 7.15-6.60 (m, 2H, 2 x ArH), 4.10 (bs, 2H, $ArCH_2Ar$).

70. bis(pentafluorophenyl)methane (172)

To a stirred mixture of pentafluorobenzene 6.44g (38.3 mmols) and aluminium chloride 0.511g (3.83 mmols) was added dropwise 2,3,4,5,6-pentafluorobenzyl bromide 1g (3.83 mmols), at room temperature. Stirring continued for 1 hour, the mixture was refluxed for 20 hours and poured onto ice-hydrochloric acid, the organic phase was extracted with dichloromethane (50 ml) and washed with water (50 ml). The solvent was then removed and the solid material was treated with cold ethanol and filtered. The solvent was then removed and the residue recrystallised from hexane 0.4377g (32.8%) m.pt. 63-64°C. Found: C, 44.97; H, 0.51% $C_{13}F_{10}H_2$ requires C, 44.83; H, 0.57%; δ_H (90 MHz, $CDCl_3$) 4.06(bs, 2H, $ArCH_2Ar$); ν_{max} (KBr disc) 1659(m), 1523(s), 1501(s), 1132(m), 1116(m), 1028(s), 981(s), 972(m), 895(m), 630(w), cm^{-1} ; MS m/e 348 (M^+), 329, 279, 229, 181, 117, 93 69.

71. Bis(pentakis(phenylthio)phenylmethane (176)

Sodium phenylthiolate 0.71g (5.75 mmols), prepared from thiophenol and sodium according to the method of experiment 16 (Method A), was reacted with decafluorodiphenylmethane 0.100g (0.29 mmols) in DMEU (30 ml), at 60 °C for 3 days and worked up according to the method of experiment 43. The yellow oil was purified by gravity column, pet. ether (40-60°C)/diethyl ether [1:1] to yield pale yellow crystals 0.166g (46.4%) m.pt. 181-182°C. TLC R_f = 0.42 pet. ether (40-60°C)/diethyl ether [1:1]; δ_H (200 MHz, $CDCl_3$) 7.12-6.67 (m, 50H, 50 x ArH), 5.10 (bs, 2H, $ArCH_2Ar$); δ_C (50 MHz, $CDCl_3$) 153.55(s), 149.39(s), 145.68(s), 141.83(s), 138.10(s), 137.37(s), 128.91(d), 128.79(d), 128.72(d), 128.23(d), 127.73(d), 127.33(d), 125.75(d), 43.18(t); ν_{max} (KBr disc) 3054 (w), 3017(w), 2925(w), 1580(s), 1476(s), 1438(s), 1307(w), 1263(w), 1178(w), 1156(w), 1080(m), 1024(s), 999(w), 735(s), 698(s), 468(m) cm^{-1} ; FAB MS m/e (M^+) 1248, 1169, 1139, 1063, 1032, 955, 921, 844.

72. Bis(pentakis(cyclopentylthio)phenyl)methane (177)

Sodium cyclopentylthiolate 0.71g (5.75 mmols), prepared from cyclopentylthiol and sodium according to the method of experiment 16 (Method A), was reacted with decafluorodiphenylmethane 0.100g (0.29 mmols) in DMEU (30 ml), at 60°C, for 3 days and worked up according to the method of experiment 43. The yellow oil was purified by gravity column, pet. ether (40-60°C)/diethyl ether [15:1] to yield pale yellow crystals 67 mg (20%) m.pt. 205-210°C TLC $R_f = 0.49$ pet. ether (40-60°C)/diethyl ether [15:1]; δ_H (200 MHz, $CDCl_3$) 5.59 (bs, 2H, $ArCH_2Ar$), 3.95-3.49 (m, 10H, 10 x $ArSCH$), 1.76-1.49 (m, 80H, 40 x CH_2); δ_C (50 MHz, $CDCl_3$) 153.05(s), 147.50(s), 144.31(s), 141.56(s), 49.23(d), 48.85(d), 33.08(t), 32.85(t), 24.96(t), 24.82(t); ν_{max} (KBr disc) 2955 (s), 2866(s), 1448(m), 1384(w), 1317(m), 1289(m), 1236(m), 1128(w), 1082(w), 954(w), 933(w), 902(w) cm^{-1} ; FAB MS m/e (M^+) 1288, 1287.

73. 1,2-Bis(pentakis(phenylthio)phenyl)ethane (179)

Sodium phenylthiolate 0.545g (4.13 mmols) prepared from thiophenol and sodium according to the method of experiment 16 (Method A), was reacted with 1,2-bis(pentabromophenyl)ethane 0.200g (0.21 mmols) in DMEU (30 ml), at 60°C, for 3 days and worked up according to the method of experiment 43. The yellow oil was purified by gravity column, pet. ether (40-60°C)/diethyl ether [1:1] to yield yellow crystals 0.210g (80.9%) m.pt. 218-220°C. TLC R_f = 0.41 pet. ether (40-60°C)/diethyl ether [1:1]; δ_H (200 MHz, $CDCl_3$) 7.13-6.83 (m, 50H, 50 x ArH), 3.86 (bs, 4H, $ArCH_2CH_2Ar$); δ_C (50 MHz, $CDCl_3$) 152.20(s), 150.79(s), 146.39(s), 141.20(s), 138.10(s), 138.01(s), 129.02(d), 128.75(d), 128.66(d), 128.06(d), 126.55(d), 125.74(d), 125.52(d), 125.16(d), 37.30(t); ν_{max} (KBr disc) 3068(m), 3054(m), 1582(s), 1476(s), 1438(s), 1306(w), 1176(w), 1080(m), 1068(w), 730(s), 705(m), 680(s) cm^{-1} .

74. 1,2-Bis(pentakis(*p*-methylphenylthio)phenyl)ethane (180)

Sodium *p*-methylphenylthiolate 1.2g (8.23 mmols), prepared from *p*-methylthiophenol and sodium according to the method of experiment 16 (Method A), was reacted with 1,2-bis(pentabromophenyl)ethane, 0.400g (0.41 mmols) in DMEU (30 ml), at 60°C, for 3 days and worked up according to the method of experiment 43. The yellow oil was purified by gravity column, pet ether (40-60°C)/diethyl ether [6:4] to yield yellow crystals 0.4987g (86.4%) m.pt. 210-213°C. TLC R_f = 0.43 pet. ether (40-60°C)/diethyl ether [6:4]; Found: C, 71.79; H, 5.34; S, 22.99% C₈₄H₇₄S₁₀ requires C, 71.89; H, 5.28; S, 22.82%; δ_H (200 MHz, CDCl₃) 6.95-6.71 (m, 40H, 40 x ArH), 3.82 (s, 4H, ArCH₂CH₂Ar), 2.26-2.17(3 x s, 30H, 10 x ArCH₃); δ_C (50 MHz, CDCl₃) 151.67(s), 150.66(s), 146.43(s), 141.01(s), 135.42(s), 135.28(s), 135.03(s), 134.91(s), 134.76(s), 129.68(d), 129.44(d), 129.37(d), 128.47(d), 126.69(d), 37.14(t), 21.01(q); ν_{max} (KBr disc) 3016(m), 2916(m), 2862(m), 1490(s), 1458(m), 1448(w), 1398(w), 1376(w), 1300(m), 1180(m), 1116(w), 1102(w), 1080(m), 1016(m), 800(s), 486(m) cm⁻¹.

75. 1,2-Bis(pentakis(*p*-*t*-butylphenylthio)phenyl)ethane (181)

Sodium *p*-*t*-butylphenylthiolate 1.16g (6.2 mmols), prepared from *p*-*t*-butylthiophenol and sodium according to the method of experiment 16 (Method A), was reacted with 1,2-bis(pentabromophenyl)ethane 0.300g (0.31 mmols) in DMEU (30 ml), at 60°C, for 3 days and worked up according to the method of experiment 43. The yellow oil was purified by gravity column, pet. ether (40-60°C)/diethyl ether [20:1] to yield yellow crystals 0.2734g (48.6%) m.pt. 220-225°C. TLC R_f = 0.26 pet. ether (40-60°C)/diethyl ether [20:1]; Found: C, 75.20; H, 7.49; S, 17.39% $C_{114}H_{134}S_{10}$ requires C, 75.08; H, 7.35; S, 17.56%; δ_H (200 MHz, $CDCl_3$) 7.16-6.73 (m, 40H, 40 x ArH), 3.79 (s, 4H, $ArCH_2CH_2Ar$), 1.25-1.16 (3 x s, 90H, 10 x $C(CH_3)_3$); δ_C (50 MHz, $CDCl_3$) 152.69(s), 150.74(s), 148.33(s), 148.27(s), 142.05(s), 135.31(s), 134.99(s), 134.71(s), 127.85(d), 127.71(d), 126.55(d), 125.84(d), 125.64(d), 34.30(s), 34.30(s), 31.28(q); ν_{max} (KBr disc) 2960(s), 2902(m), 2866(m), 1496(s), 1460(m), 1396(m), 1362(m), 1268(m), 1118(m), 1012(m) cm^{-1} .

76. 1,2-Bis(pentakis(3,5-dimethylphenylthio)phenyl)ethane (182)

Sodium 3,5-dimethylphenylthiolate 0.99g (6.2 mmols), prepared from 3,5-dimethylthiophenol and sodium according to the method of experiment 16 (Method A), was reacted with 1,2-bis(pentabromophenyl)ethane 0.300g (0.31 mmols) in DMEU (30 ml), at 60°C, for 3 days and worked up according to the method of experiment 43. The yellow oil was purified by gravity column, pet. ether (40-60°C)/diethyl ether [9:1] to yield yellow crystals 0.360g (75.6%) m.pt. 90-94°C; TLC R_f = 0.20 pet. ether (40-60°C)/diethyl ether [9:1]; Found: C, 73.15; H, 6.27; S, 20.99% $C_{94}H_{94}S_{10}$ requires C, 73.15; H, 6.09; S, 20.76%; δ_H (200 MHz, $CDCl_3$) 6.63-6.48 (m, 20H, 20 x ArH), 6.36 (s, 10H, 10 x ArH), 3.65(bs, 4H, $ArCH_2CH_2Ar$), 2.11-2.09 (2 x s, 60H, 20 x $ArCH_3$); δ_C (50 MHz, $CDCl_3$) 154.18(s), 150.54(s), 146.05(s), 141.76(s), 138.12(s), 138.05(s), 137.86(s), 127.41(d), 126.95(d), 125.54(d), 125.14(d), 123.73(d), 37.00(t), 21.27(q), 21.26(q); ν_{max} (KBr disc) 3029(w), 3002(w), 2946(m), 2914(m), 2857(m), 1600(s), 1579(s), 1461(m), 1375(m), 1305(w), 1260(w), 1036(w), 834(s), 682(s) cm^{-1} .

77. 1,2-Bis(cyclohexylthio)phenyl)ethane (183)

Sodium cyclohexylthiolate 0.851g (6.17 mmols), prepared from cyclohexylthiol and sodium according to the method of experiment 16 (Method A), was reacted with 1,2-bis(pentabromophenyl)ethane 0.300g (0.31 mmols) in DMEU (30 ml), at 60°C, for 3 days and worked up according to the method of experiment 43. The pale yellow oil was purified by graduated flash column from pet. ether (40-60°C) to diethyl ether to yield an off-white solid 0.2646g (64.9%). TLC R_f = 0.31 pet. ether (40-60°C)/diethyl ether [20:1]; δ_H (200 MHz, $CDCl_3$) 3.68-3.10 (m, 14H, $ArCH_2CH_2Ar$, $ArSCH$), 2.10-1.21 (m, 80H, 40 x CH_2); δ_C (50 MHz, $CDCl_3$) 152.30(s), 147.45(s), 139.96(s), 49.56(d), 49.23(d), 47.92(d), 33.14(t), 33.02(t), 32.94(t), 26.26(t), 25.89(t); ν_{max} (KBr disc) 2927(s), 2851(s), 1448(w), 1339(w), 1300(w), 1261(m), 1200(w), 1178(w), 1095(w), 1048(w), 1027(w), 997(w), 887(w), 8161(w), 737 cm^{-1} .

78. Attempted formation of 1,2-Bis(pentakis(cyclopentylthio)phenyl)ethane

Sodium cyclopentylthiolate 0.765g (6.17 mmols), prepared from cyclopentylthiol and sodium according to the method of experiment 16 (Method A), was reacted with 1,2-bis(pentabromophenyl)ethane 0.300 mg (0.31 mmols) in DMEU (30 ml), at 60°C, for 2 days and worked up according to the method of experiment 43. The dark oil contained 3 spots by TLC, pet. ether (40-60°C) /diethyl ether [20:1], none of which could be isolated and no further analysis was done.

79. 1,6-Bis(pentakis(phenylthio)phenyl)hexa-1,6-dione (185)

Sodium phenylthiolate 0.5417g (4.1 mmols) prepared from thiophenol and sodium according to the method of experiment 16 (Method A), was reacted with 1,6-bis(pentachlorophenyl)hexa-1,6-dione 0.100g (0.16 mmols) in DMEU (30 ml), at room temperature, for 4 days and worked up according to the method of experiment 43. The resulting oil was purified by gravity column pet. ether (40-60°C)/diethyl ether [6:4] to yield off-white crystals 0.147g (22.0%) m.pt. 131-133°C. TLC R_f = 0.27 pet. ether (40-60°C)/diethyl ether [6:4]; δ_H (200 MHz, $CDCl_3$) 7.30-6.82 (m, 50H, 50 x ArH), 2.70 (bs, 4H, 2 x ArC(O)CH₂), 1.68(bs, 4H, 2 x CH₂); δ_C (50 MHz, $CDCl_3$) 154.82(s), 150.55(s), 148.98 (s), 137.51(s), 137.08(s), 136.52(s), 134.80(s), 129.16(d), 128.89(d), 128.79(d), 128.18(d), 127.56(d), 126.37(d), 126.24(d), 43.55(t), 22.35(t); ν_{max} (KBr disc) 3070 (w), 3056(w), 3018(w), 2932(w), 2872(w), 1581(s), 1581(s), 1477(s), 1439(s), 1287(w), 1194(w), 1179(m), 1081(m), 1068(m), 1024(s), 999 (w), 736(s), 699(s), 686(s), cm^{-1} ; FAB MS (M+H)⁺ 1347, 1268, 1175, 1115.

80. Reaction of sodium phenylthiolate with bis(pentachlorophenyl)-
1,1,2,2-tetramethyldisilane (186)

Sodium phenylthiolate (0.644g (4.88 mmols), prepared from thiophenol and sodium according to the method of experiment 16 (Method A), was reacted with bis(pentachlorophenyl)-1,1,2,2-tetramethyldisilane 0.100g (0.16 mmols) in DMEU (30 ml), at 60°C, for 22 hours and worked up according to the method of experiment 43. The brown oil was purified by gravity column, pet. ether (40-60°C)/diethyl ether [6:4] to give a white solid which was recrystallised from chloroform/ethanol 82 mg (81.6%). m.pt. 138°C. TLC R_f = 0.37, pet. ether (40-60°C)/diethyl ether [6:4]; Found: C, 69.90; H, 4.21% C₃₆H₂₅S₅ requires C, 69.96; H, 4.32; δ_H (200 MHz, CDCl₃) 7.24-7.02 (m, 25H, 25 x ArH), 6.15 (s, 1H, Ar_{core}H); δ_C (50 MHz, CDCl₃) 151.92(s), 148.47(s), 137.94(s), 136.79(s), 135.43(d), 130.55(s), 130.36(s), 129.75(d), 129.49(d), 128.85(d), 128.76(d), 127.99(d), 126.86(d), 125.61(d), 123.57(d); ν_{max} (KBr disc) 3054(s), 1578(s), 1518(m), 1476(s), 1439(s), 1368(w), 1296(w), 1279(w), 1082(w), 1022(m), 999(w), 748(m), 737(s), 704(m), 687(s) cm⁻¹; MS m/e 618 M⁺ 508, 400, 322, 290, 258, 214, 110, 77.

81. D₂O Quench

Sodium phenylthiolate, 0.590g (4.47 mmols), was reacted with bis(pentachlorophenyl)-1,1,2,2-tetramethyldisilane 0.100g (0.16 mmols) in DMEU (30 ml), as before. The reaction was then quenched with D₂O (10 ml) and then worked up according to the method of experiment 43. The resulting oil was purified as before to give a white solid m.pt. 137-138°C. TLC R_f = 0.37, pet. ether (40-60°C)/diethyl ether [6:4]; δ_H (200 MHz, CDCl₃) 7.24-7.02 (m, 25H, 25 ArH), 6.15 (s, 1H, Ar_{core}H).

82. 4-Biphenyltrimethylsilane (190)

To a 100 ml 3-necked flask equipped with a dropping funnel, a reflux condenser and containing 0.200g of magnesium, a crystal of iodine and THF (25 ml) was added 5 ml of a solution containing 4-bromobiphenyl 2.0g (8.58 mmols) in THF (40 ml). Once all the iodine had disappeared, the rest of the solution was added drop by drop and stirred until all magnesium has disappeared, trimethylchlorosilane (2 ml) is added dropwise and then refluxed for 12 hours. The mixture was then washed with ammonium chloride solution taken up in diethyl ether and washed with brine and dried with sodium sulphate. The solvent was removed and the resulting white solid was purified by gravity column, pet. ether (40-60°C) and distillation at 0.05 mm (110°C) to yield a white solid 0.586g (30.2%), m.pt. 49-50°C; δ_{H} (90 MHz, CDCl_3) 7.75-7.50 (m, 9H, 9 x ArH), 0.33 (s, 9H, $\text{Si}(\text{CH}_3)_3$); MS m/e 226 M^+ , 211, 195, 181, 165, 152, 105.

83. Reaction of sodium phenylthiolate with 4-biphenyltrimethylsilane (190)

Sodium phenylthiolate 0.26g (1.97 mmols), prepared from thiophenol and sodium according to the method of experiment 16 (Method A), was reacted with 4-biphenyltrimethylsilane 70 mg(0.31 mmols) in DMEU (20 ml), at 60°C, for 2 days and worked up according to the method of experiment 43. The resultant oil was purified by gravity column pet. ether (40-60°C), this gave the starting material back as a white solid; δ_{H} (90 MHz, CDCl_3) 7.75-7.50 (m, 9H, 9 x ArH), 0.33 (s, 9H, $\text{Si}(\text{CH}_3)_3$).

84. Reaction of potassium chloride with 4-biphenyltrimethylsilane (190)

Potassium chloride 0.165g (2.2 mmols) and 18-crown-6 0.584g (2.2 mmols) were added to DMEU (20 ml) and the sample is degassed. 4-Biphenyltrimethylsilane 0.100g (0.44 mmols) was then added to the reaction mixture and the sample degassed again, and it is stirred for 1 day, at 60°C, and worked up according to the method of experiment 43. The resultant oil was purified by gravity column, pet. ether (40-60°C). This gave the starting material back as a white solid; δ_H (90 MHz, $CDCl_3$) 7.75-7.50 (m, 9H, 9 x ArH), 0.33 (s, 9H, $Si(CH_3)_3$).

85. Reaction of sodium phenylthiolate with bis(pentachlorophenyl)-
1,1,2,2,3,3-hexamethyltrisilane (191)

Sodium phenylthiolate, 0.295g (2.23 mmols), prepared from thiophenol and sodium according to the method experiment 16 (Method A), was reacted with bis(pentachlorophenyl)-1,1,2,2,3,3-hexamethyltrisilane 0.050g (7.4×10^{-2} mmols) in DMEU (30 ml), at 60°C, for 22 hours and worked up according to the method of experiment 43. The brown oil was purified by gravity column, pet. ether (40-60°C)/diethyl ether [6:4] to give a white solid which was recrystallised from chloroform/ethanol 49.6 mg (54.0%) m.pt. 136-138°C. TLC R_f = 0.38, pet. ether (40-60°C)/diethyl ether; δ_H (90 MHz, $CDCl_3$) 7.25-7.00 (m, 25H, 25 x ArH), 6.20 (s, 1H, Ar_{core}H).

Another product was isolated from the column, a white solid 3.7 mg (3.8%) TLC R_f = 0.48, pet. ether (40-60°C)/diethyl ether, [6:4]; δ_H (200 MHz, $CDCl_3$) 7.47-7.44 (m, 10H, 10 x ArH), 6.92 (s, 2H, 2 x Ar_{core}H); MS m/e 361.9743 M^+ $C_{18}H_{12}Cl_2S_2$ requires 361.9767.

86. Reaction of sodium phenylthiolate with pentafluorophenyl trimethylsilane (192)

Sodium phenylthiolate, 0.825g (6.25 mmols), prepared from thiophenol and sodium according to the method of experiment 16 (Method A), was reacted with pentafluorophenyltrimethylsilane 0.100g (0.42 mmols) in DMEU (30 ml), at 60°C, for 22 hours and worked up according to the method of experiment 43. The brown oil was purified by gravity column, pet. ether (40-60°C/diethyl ether [6:4]) to give a white solid which was recrystallised from chloroform/ethanol 98 mg (53.6%) m.pt. 138°C. TLC R_f = 0.37 pet. ether (40-60°C)/diethyl ether [6:4]; δ_H (200 MHz, $CDCl_3$) 7.30-6.90 (m, 25H, 25 x ArH), 6.15 (s, 1H, $Ar_{core}H$).

87. Reaction of pentafluorophenyltrimethylsilane (192)
and pentafluorobenzylbromide (197)

With KF and 18-Crown-6

Pentafluorophenyltrimethylsilane 150 mg (0.625 mmols), pentafluorobenzylbromide 245 mg (0.939 mmols), potassium fluoride 72 mg (1.24 mmols) and 18-Crown-6 265 mg (1.00 mmols) were added to degassed DMEU (10 ml) and the mixture degassed. The reaction was heated to 60°C and left overnight. It was worked up by adding pet. ether (40-60°C) (100 ml) and washing with water (3 x 100 ml). Upon removal of the solvent a flash chromatography (pet. ether 40-60°C) a white solid was obtained 46.5 mg (21.5%); δ_{H} (90 MHz, CDCl_3) 4.06(bs, 2H, ArCH_2Ar); MS m/e 348 M^+ , 329, 309, 278, 181.

Without KF and 18-Crown-6

Pentafluorophenyltrimethylsilane 150 mg (0.625 mmols) and pentafluorobenzylbromide 245 mg (0.939 mmols) were added to degassed DMEU (20 ml) and the mixture degassed. The reaction was heated, at 60°C, overnight and worked up as before, to give back starting materials.

88. Pentakis(phenylthio)benzene (188)

Sodium phenylthiolate 2.357g (17.9 mmols), prepared from thiophenol and sodium according to the method of experiment 16 (Method A), was reacted with pentafluorobenzene 0.200g (1.19 mmols) in DMEU (30 ml), at 60°C, for 2 days and worked up according to the method of experiment 43. The resultant oil was purified by gravity column pet. ether (40-60°C)/diethyl ether [6:4], and the solid obtain recrystallised from chloroform/ethanol, to give off-white crystals, 0.368g (50.0%) m.pt. 137-138°C; δ_{H} (90 MHz, CDCl_3) 7.2-7.0 (m, 25H, 25 x ArH), 6.15 (s, 1H, $\text{Ar}_{\text{core}}\text{H}$).

89. Pentakis(*p*-methylphenylthio)benzene (199)

Sodium *p*-methylphenylthiolate, 1.3g (8.9 mmols), prepared from *p*-methylphenylthiol and sodium according to the method of experiment 16 (Method A), was reacted with pentafluorobenzene 0.100g (0.60 mmols) in DMEU (30 ml), at 60°C, for 2 days and worked up according to the method of experiment 43. The resultant oil was purified by gravity column, pet. ether (40-60°C)/diethyl ether [7:3] to yield off-white crystals 0.1773g (43.3%) m.pt. 166-168°C. TLC R_f = 0.40 pet. ether (40-60°C)/diethyl ether [7:3]; δ_H (200 MHz, $CDCl_3$) 7.11-6.90 (m, 20H, 20 x ArH), 6.21 (s, 1H, Ar_{core}H), 2.36 (s, 6H, 2 x ArCH₃), 2.27 (s, 6H, 2 x ArCH₃), 2.23 (s, 3H, ArCH₃); δ_C (50 MHz, $CDCl_3$) 151.74(s), 148.82(s), 129.13(s), 139.07(s), 135.38(d), 134.48(s), 133.34(s), 130.44(d), 130.19(d), 129.58(d), 129.46(d), 128.45(d), 127.54(d), 127.10(d), 123.44(d), 21.48(q), 21.00(q); ν_{max} (KBr disc) 2030(m), 2915(m), 1595(w), 1516(m), 1487(s), 1300(w), 1181(m), 1090(m), 1021(m), 811(s), 805(s), 500(m) cm^{-1} .

90. Pentakis(*p*-*t*-butyl phenylthio)benzene (200)

Sodium *p*-*t*-butylphenylthiolate 1.12g (5.96 mmols), prepared from *p*-*t*-butylphenylthiol and sodium according to the method of experiment 16 (Method A), was reacted with pentafluorobenzene 0.100g (0.60 mmols) in DMEU (30 ml), at 60°C, for 2 days and worked up according to the method of experiment 43. The resultant oil was purified by gravity column pet. ether (40-60°C)/diethyl ether [20:1] and the solid recrystallised from hexane/diethyl ether to give white crystals 0.347g (64.9%) m.pt. 173-175°C. Found: C, 74.93; H, 7.32; S, 17.97% $C_{56}H_{66}S_5$ requires C, 74.83; H, 7.35; S, 17.82%; δ_H (200 MHz, $CDCl_3$) 7.25-6.94 (m, 20H, 20 x ArH), 6.66 (s, 1H, Ar_{core}H), 1.64-0.88 (3 x s, 45H, 5 x C(CH₃)₃); δ_C (50 MHz, $CDCl_3$) 151.87(s), 150.03(s), 148.69(s), 134.25(d), 133.74(s), 129.29(d), 128.20(d), 127.31(d), 126.41(d), 125.87(d), 125.78(d), 34.60(s), 34.46(s), 31.28(q); ν_{max} (KBr disc) 2962(s), 2900(m), 2866(m), 1520(w), 1494(s), 1482(m), 1460(w), 1396(w), 1262(m), 1290(w), 1268(m), 1116(m), 1012(m), 822(s), 558(w), 544(w) cm^{-1} .

91. Pentakis(3,5-dimethylphenylthio)benzene (201)

Sodium 3,5-dimethylphenylthiolate 0.95g (5.94 mmols), prepared from 3,5-dimethylphenylthiol and sodium according to the method of experiment 16 (Method A), was reacted with pentafluorobenzene 0.100g (0.60 mmols) in DMEU (30 ml), at 60°C, for 2 days and worked up according to the method of experiment 43. The resultant oil was purified by flash chromatography toluene/pet. ether (40-60°C) [3:7] and recrystallised from chloroform/methanol to yield white crystals 0.361g (80.0%) m.pt. 199-200°C. TLC R_f = 0.40 pet. ether (40-60°C)/diethyl ether [8:2]; Found: C, 72.70; H, 6.22% C₄₆H₄₆S₅ requires C, 72.82; H, 6.07%; δ_H (200 MHz, CDCl₃) 6.85-6.63 (m, 15H, 15 x ArH), 6.17 (s, 1H, Ar_{core}H), 2.21-2.13 (3 x s, 30H, 10 x ArCH₃); δ_C (50 MHz, CDCl₃) 152.04(s), 138.95(s), 138.20(s), 138.02(s), 127.19(s), 136.36(s), 132.97(d), 131.01(d), 130.21(s), 127.56(d), 127.40(d), 126.12(d), 124.25(d), 123.88(d), 21.38(q), 21.24(q), 21.15(q); ν_{max} (KBr disc) 2928(s), 2851(s), 1512(m), 1477(w), 1447(m), 1338(w), 1261(m), 1198(w), 996(w), cm⁻¹.

92. Pentakis(cyclohexylthio)benzene (202)

Sodium cyclohexylthiolate 0.821g (5.96 mmols), prepared from cyclohexylthiol and sodium according to the method of experiment (Method A), was reacted with pentafluorobenzene 0.100g (0.60 mmols) in DMEU (30 ml), at 60°C, for 2 days and worked up according to the method of experiment 43. The resultant oil was purified by gravity column pet. ether (40-60°C)/diethyl ether [20:1] to give a white solid powder 0.2292g (59.4%). TLC R_f = 0.29 pet. ether (40-60°C)/diethyl ether [20:1]; δ_H (200 MHz, $CDCl_3$) 6.93 (s, 1H, $Ar_{core}H$), 3.41-3.07 (m, 5H, 5 x $ArSCH_2$), 2.14-1.22 (m, 50H, 25 x CH_2); δ_C (50 MHz, $CDCl_3$) 149.59(s), 146.18(s), 132.78(s), 120.16(d), 50.22(d), 48.90(d), 44.65(d), 33.22(t), 32.98(t), 25.37(t), 26.16(t), 26.09(t), 25.78(t); ν_{max} (KBr disc) 2927(s), 2850(s), 1518(m), 1447(m), 1260(m), 1198(w), 996(m), 886(w), 856(w), 844(w), 816(w), 800(w), 736(w), cm^{-1} .

93. Pentakis(10-(*S*)-camphorthio)benzene (203)

To a solution of sodium 10-*S*-camphorthiolate in DMEU (30 ml), prepared from 10-*S*-mercaptocamphor 10.09g (5.96 mmols) and sodium hydride (95%) 0.157g (6.21 mmols) according to the method of experiment 16 (Method B), was added pentafluorobenzene 0.100g (0.60 mmols) and stirred, at 60°C, for 2 days. It was then worked up according to the method of experiment 43. The oil was purified by gravity column diethyl ether to yield a white powder 0.181g (30.8%) m.pt. 145-147°C. TLC R_f = 0.42, diethyl ether; Found: C, 67.79; H, 7.71; S, 16.40%. $C_{56}H_{76}O_5S_5$ requires C, 68.02; H, 7.70; S, 16.19%; δ_H (200 MHz, $CDCl_3$) 6.98 (s, 1H, $Ar_{core}H$), 3.31-2.76 (m, 10H), 2.49-1.80 (m, 25H, 25 x alkylH), 1.62-1.26 (m, 10H, 10 x alkylH), 1.17-0.96 (m, 30H, 10 x CH_3); δ_C (50 MHz, $CDCl_3$) 217.02(s), 216.86(s), 216.44(s), 150.44(s), 148.31(s), 133.82(s), 119.60(d), 61.19(s), 60.89(s), 60.28(s), 48.04(s), 47.89(s), 43.44(d), 43.29(d), 43.08(t), 43.01(t), 36.67(t), 34.51(t), 129.28(t), 26.96(t), 26.56(t), 26.41(t), 26.26(t), 20.61(q), 20.29(q), 20.05(q); ν_{max} (KBr disc) 2958(s), 2884(m), 1742(s), 1452(w), 1416(w), 1390(w), 1372(w), 1048(m) cm^{-1} .

94. Hexakis(*p*-methoxyphenoxy)benzene (68)

Sodium *p*-methoxyphenolate 81.19g (0.556 moles), prepared from *p*-methoxyphenol and sodium hydride (95%) according to the method of experiment 17, was reacted with hexafluorobenzene 5.74g (30.9 mmols) in DMEU (500 ml), at 90°C, for 1 month and worked up by adding water (*ca.* 1l) and filtering off the solid. The solid was then washed with water, then ethanol before recrystallisation from chloroform/methanol, to give white crystals 14.19g (56.8%) m.pt. 233-235°C; δ_H (90 MHz, $CDCl_3$) 6.65 (s, 24H, 24 x ArH), 3.70 (s, 18H, 6 x $ArOCH_3$); M.S. m/e 810 M^+ .

95. Hexakis(*p*-hydroxyphenoxy)benzene (69)

To a solution of hexakis(*p*-methoxyphenoxy)benzene 1.0g (1.23 mmols) in freshly distilled dichloromethane (100 ml), under a nitrogen atmosphere and cooled to -78°C , was injected boron tribromide *ca.* 4.7 ml (49.2 mmols). The reaction was then allowed to rise slowly to room temperature and stirred for 12 hours. Water was then carefully added (1 drop at a time) until no more fumes were given off. The resulting precipitate was then filtered off, and washed with water and then cold ethanol and dried over P_2O_5 to yield a white powder 0.89g (99%) m.pt. $320\text{-}325^{\circ}\text{C}(\text{dec})$; δ_{H} (200 MHz, $\text{d}^6\text{-DMSO}$) 9.03 (s, 6H, 6 x ArOH), 6.55 (s, 24H, 24 x ArH); ν_{max} (KBr disc) 3229 (br,s), 2689 (br,w), 1505 (s), 1453(s), 1360(m), 1281(w), 1194(s), 1098(m), 1011(m), 997(s), 852(w), 841(m), 828(m), 781(w), 669(w), 625(w), 534(w), 527(w), cm^{-1} .

96. Attempted linking of hexakis(*p*-hydroxyphenoxy)benzene arm

Acetic Acid.

Hexakis(*p*-hydroxyphenoxy)benzene 0.4996g (0.69 mmols) was added to acetic acid (50 ml) and refluxed. While refluxing 2,6-bis(bromomethyl)-4-methylphenol 1.235g (4.2 mmols) in acetic acid (100 ml) was added over 4 hours with vigorous stirring. The solution was then refluxed for a further 48 hours. The acetic acid was removed to leave a green solid which contained a mixture of compounds, none of which could be isolated. No further analysis was done.

Acetic Acid High Dilution.

Hexakis(*p*-hydroxyphenoxy)benzene 0.100g (0.14 mmols) was added to acetic acid (1l) and refluxed until all the compound had dissolved. Then, 2,6-bis(bromomethyl)-4-methylphenol 0.244g (0.83 mmols) in acetic acid (40 ml) was added over 6 hours and the reaction was refluxed for 2 days. A further portion of 2,6-bis(bromomethyl)-4-methylphenol 0.122g (0.41 mmols) in acetic acid (20 ml) was added over 3 hours and the reaction was refluxed for a further 2 days. The acetic acid was then removed to leave a brown solid which

contained a mixture of compounds, seen by TLC toluene/methanol [19:1] none of which could be isolated. No further analysis was carried out.

Titanium tetrachloride in 1,4-dioxane.

Hexakis(*p*-hydroxyphenoxy)benzene 0.50g (0.69 mmols) was refluxed in 1,4-dioxane (55 ml) until all the material had dissolved. 2,6-Bis(bromomethyl)-4-methylphenol 1.215g (4.13 mmols) in 1,4-dioxane (14 ml) was then added over 2 hours and the reaction refluxed for 3 days. The 1,4-dioxane was then removed to yield a brown solid which could not be purified any further. No further analysis was done.

KOH in xylene.

Hexakis(*p*-hydroxyphenoxy)benzene 0.500g (0.69 mmols) was added to xylene (20 ml) containing 1.6M KOH (1 ml), under a nitrogen atmosphere, in a 100ml flask equipped with a Dean Stark collector. 2,6-bis(hydroxymethyl)-4-methylphenol 0.810g (4.82 mmols) was added after about one hour's reflux and the reaction was left to reflux overnight. The xylene was then removed to leave a brown solid which could not be purified any further. No further analysis was carried out.

97. H₂ inclusion in hexakis(*p*-hydroxyphenoxy)benzene

Hexa(*p*-hydroxyphenoxy)benzene 1.5g (1.30 mmols) was added to dry ethanol (50 ml) in a hydrogenation vessel. The vessel was then placed in the high pressure hydrogenator. The hydrogenator was then degassed filled with hydrogen and degassed again, it was then refilled with hydrogen to a pressure of 1500 psi and shaken for 15 hours at 230°C (pressure rose to 2700 psi). The hydrogenator was then allowed to cool and sit for 1 week, it was then degassed and the vessel removed. The resulting crystals are filtered and dried m.pt. >330 °C.

98. Attempted inclusion of H_2S in hexakis(*p*-hydroxyphenoxy)benzene

Hexakis(*p*-hydroxyphenoxy)benzene was dissolved up in a benzoalcohol (35 ml) in a sealed tube. The solution was then transferred to a 3-necked flask equipped with a dropping funnel, a condenser and a gas bleed. H_2S was bubbled through the mixture for 15 mins., was then added and the mixture rebubbled with H_2S for 1 hour. The sample was purged with nitrogen to remove excess H_2S and then filtered to leave a white powder. Microanalysis shows little or no inclusion of H_2S .

99. 2,6-Bis(bromomethyl)-4-methylphenol (207)

2,6-Bis(hydroxymethyl)-4-methylphenol 3.9g (23.2 mmols) was added to HBr/acetic acid (30%) (20 ml). After about 5 minutes (once it had dissolved and reprecipitated) it was taken out dissolved in ethyl acetate and the acetic acid removed to give a white solid which was recrystallised from pet. ether (40-60°C) to yield white crystals 3.97g (66.29%) m.pt. 119-120°C, TLC R_f = 0.51, toluene; δ_H (200 MHz, $CDCl_3$) 7.07 (s, 2H, 2 x ArH), 5.44 (s, 1H, ArOH), 4.52 (s, 4H, 2 x ArCH₂Br), 2.25 (s, 3H, ArCH₃); δ_C (50 MHz, $CDCl_3$) 151.9(s), 131.9(d), 130.7(s), 125.0(s), 29.6(t), 20.3(q); MS m/e 296 M⁺, 213, 133, 105, 91, 79, 63.

100. Hexakis(3,5-dimethoxyphenoxy)benzene (211)

Sodium 3,5-dimethoxyphenolate, 11.43g (64.9 mmols) prepared from 3,5-dimethoxyphenol and sodium hydride (95%) according to the method of experiment 17, was reacted with hexafluorobenzene 0.8056g (4.33 mmols) in DMEU (50 ml), at 90°C, for 1 month, and worked up according to the method of experiment 43. The brown oil was purified by gravity column, diethyl ether and resulting solid was recrystallised from chloroform/methanol to give white crystals 1.345g (31.4%) m.pt. 159-160°C. Found: C, 65.53; H, 5.66%. $C_{54}H_{54}O_{18}$ requires C, 65.45; H, 5.45%; δ_H (200 MHz, $CDCl_3$) 6.15 (t, $J=2.1$ Hz, 6H, 6 x ArH), 5.91 (d, $J=2.1$ Hz, 12H, 12 x ArH), 3.63 (s, 36H, 12 x $ArOCH_3$); δ_C (50 MHz, $CDCl_3$) 161.70(s), 159.64(s), 140.69(s), 95.39(d), 94.85(d), 55.66(q); ν_{max} (KBr disc) 3007(w), 2961(m), 2837(w), 1624(s), 1591(s), 1481(m), 1457(s), 1441(m), 1280(w), 1206(m), 1196(s), 1155(s), 1131(s), 1062(m), 1056(m), 1030(m), 821(m), 814(m), cm^{-1} ; FAB MS m/e $(M+H)^+$ 991.3354 ($C_{54}H_{54}O_{18} + H^+$ requires 991.3388).

101. Attempted formation of Hexakis(3,5-dihydroxyphenoxy)benzene
(210) with Boron Tribromide

To a solution of hexakis(3,5-dimethoxyphenoxy)benzene 2.18g (2.2 mmols) in freshly distilled dichloromethane (150 ml), under a nitrogen atmosphere and cooled to -78°C , was added Boron tribromide 25 ml (0.264 moles). The reaction was then allowed to warm up to room temperature and stirred for 12 hours. Water was then carefully added (1 drop at a time) until no more fumes were given off. The resulting precipitate was then filtered off and taken up in methanol. The resulting solution showed many spots on TLC methanol/ethyl acetate [1:9] none of which could be separated. No further analysis was carried out.

102. Attempted Formation of Hexakis(3,5-dihydroxyphenoxy)benzene (210)
with pyridinium chloride

Excess pyridinium chloride 1.17g (10.1 mmols) and hexakis (3,5-dimethoxyphenoxy)benzene 0.200g (0.202 mmols) were stirred and heated to 190°C for 3 hours. The resulting hot dark syrup was poured into HCl 3M (50 ml) and stirred for 10 minutes. The mixture was then filter-washed with dichloromethane, dissolved in methanol and dried with sodium sulphate. The methanol was then removed to leave a white solid which contained a mixture of products, shown on TLC, methanol/ethyl acetate [1:9] none of which could be isolated. No further analysis was carried out.

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